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# MODERN CHEMISTRY

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## PREFACE

AN intensive knowledge of chemistry may lead into such specialized and highly practical commercial fields that the layman is prone to overlook the fact that this science also has a place in the curriculum of culture. Yet this is true by very virtue of the prominent part played by chemistry in modern life. The daily press, magazines, and writings with a greater claim to a place as literature, may all be read with keener understanding and appreciation if the many scientific references or implications they usually contain are intelligible to us. And as we may become better readers through some chemical knowledge, likewise may we be more intelligent talkers and listeners when conversation turns to automobiles or the radio; paints, lacquers, or alloy steels; foodstuffs, rayon, cellophane, drugs, or medicines.

Chemistry is of cultural value also in that as a study it develops the reasoning power and improves the memory. It demands the precision of mathematics, and an exactness of words and endings comparable to the study of a foreign language. And analogies of discipline and government may be drawn from the fact that no subject shows more clearly that the characteristics and behavior of the mass depend upon the relationship and arrangement of its minute particles.

The aim has been to make this book practical without neglecting the fundamental principles upon which the science is based. For that reason the relation of chemistry to water purification, fuels and illuminants, agriculture, paints and varnishes, dyes, textiles, foods, and paper is especially emphasized.



The chemical processes have been selected and discussed with a view to illustrate chemical principles. A brief recital of the struggles of the men who were pioneers in chemical thought is given in an effort to humanize the subject and make it more vital. Throughout the text the author has used simple language, well within the grasp of pupils of high school age. An effort is made throughout to make the book so readable that it will be unnecessary for the instructor to spend valuable time in explaining and translating.

Especial effort has been made to develop the chemical theory in a clear, concise, logical manner. The chapters dealing with atomic theory, atomic and molecular weights, valence and chemical equations follow one another in logical order. Enough typical examples are studied in each of these chapters to give the student a clear conception of these fundamental principles as a whole. During his long teaching experience, the author has endeavored to study the mistakes which pupils are likely to make in their efforts to balance and complete equations, and in the chapter on equations to present the subject from the pupils' point of view.

A brief discussion of the electron theory of matter and of the way in which compounds are believed to be formed is given in one of the introductory chapters. In the chapter on valence, chemical attraction between elements is explained by the electron theory dealing with the gain or loss of electrons. For greater simplicity and for comparison, older concepts are used in some structural formulas. Some modern concepts of atomic structure are given in the chapter on radio-activity.

The principles of metallurgy are taught by the study of a few typical metals. The reduction of iron from its ores is studied in considerable detail as typical of the methods used for extracting tin, copper, and zinc. In like manner, the electrolysis of bauxite illustrates another important method of extracting metallic elements. The metallurgy of mag-

nesium, calcium, sodium, and potassium is too similar to need much further detailed study. Metal replacement is introduced in the chapter on hydrogen and it is then utilized in the further study of substitution reactions. The periodic table is introduced before the study of the metallic elements. This arrangement makes it possible to study elements by families or groups. The atomic numbers are printed in red, since they are of more importance in the modern table than atomic weights. The chapter on colloids includes such practical applications as the use of foam for fighting fires, froth-flotation for concentrating ores, and Cottrells for precipitating acid mist and smelter dust.

This book contains all the material needed to meet the syllabi of the College Entrance Board, of the New York State Board of Regents, or of the various cities that have revised their courses of study recently. In some schools differentiated work is now given in chemistry. Pupils who are not planning for college take a course that differs from the usual college course. In this book some topics and some chapters are starred. At the discretion of the teacher the starred topics may be omitted without affecting the unity of the course. The questions and problems are grouped into two classes. Those given in the A Groups are not too difficult for any pupil. The questions and problems given in the B Groups may be assigned as an extra group for the more capable pupils or for those who work more rapidly.

Several devices are used to enable the student to get an understanding of elementary chemistry: (1) Vocabularies are given at the beginning of each chapter; (2) The explanations are unusually full, and examples are used freely; (3) The carefully chosen illustrations help to clarify the text and to help the pupil to understand industrial processes; (4) Type problems are used to introduce all mathematical relationships; (5) The chapter summaries are carefully selected to include fundamental facts and principles; (6) Many thought-

provoking questions are appended to each chapter, and many numerical problems are included for further study.

Newark, N. J.  
*May, 1936.*

C. E. D.



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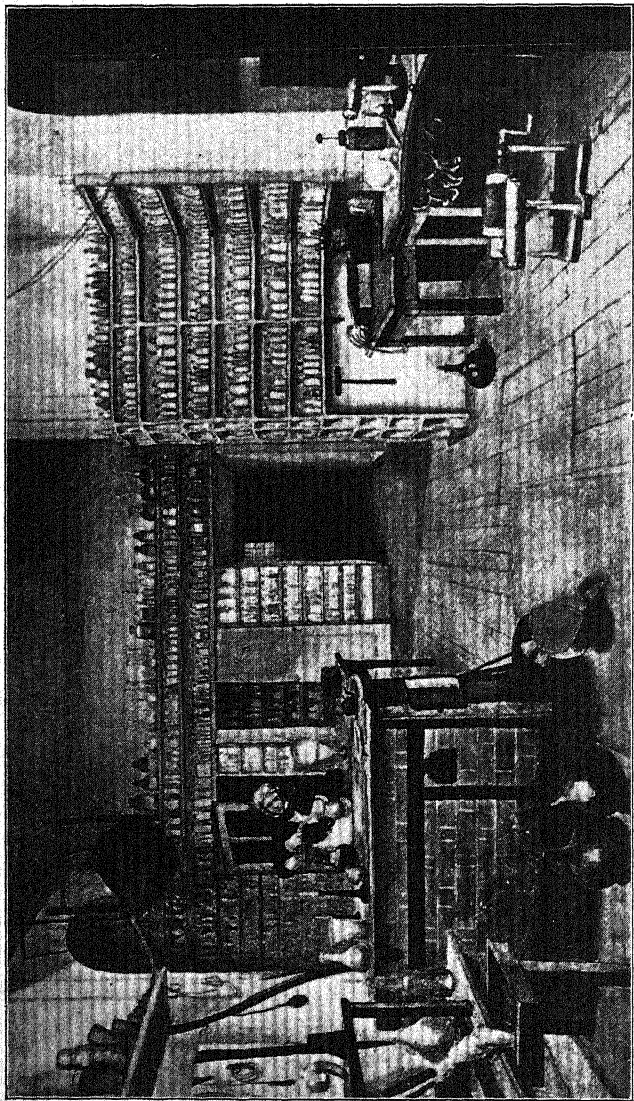
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# MODERN CHEMISTRY



*Courtesy of Fisher Scientific Co.*

When asked what he considered his greatest discovery, Sir Humphry Davy answered, "Michael Faraday."  
Here we see the illustrious Faraday at work in his laboratory.



## CHAPTER 1

# MATTER AND ENERGY

### Vocabulary

**By-product.** An additional product obtained in the manufacture of a certain product.

**Transmutation.** In alchemy, the changing of one metal into another.

**Matter.** Anything that occupies space.

**Energy.** The capacity for doing work.

**Law.** A "habit of nature," or a statement that shows how natural phenomena are related.

### A. INTRODUCTORY

**1. Chemistry — a Fundamental Science.** The science of chemistry furnishes a foundation for modern industry. In many ways it touches the life of every human being, either directly or indirectly.

*1. It explains many things about which we are naturally curious.* We observe that wood and coal will burn, if they are heated to a certain temperature. What causes them to burn, and what changes actually occur as they burn? We are all familiar with the fact that iron, silver, and some other metals tarnish, that milk sours, that foods decay, that gasoline vapor explodes when mixed with air and ignited, and that milk or water causes the formation of gas bubbles when added to baking powder. Without chemistry, there can be no explanation of any one of these familiar facts.

*2. Chemistry is closely related to other sciences.* The mineralogist and the geologist utilize chemistry in their efforts to identify the rocks and minerals of the earth's crust. The botanist finds chemistry useful in the analysis of soils and fertilizers as plant foods. Life itself is based upon many complicated chemical changes and chemical processes, and

in our universities special courses are given in bio-chemistry. One of the best of the recent books is entitled "Chemistry in Medicine." Physics is so closely related to chemistry that it is becoming increasingly difficult to study one without the other. For example, we use chemical action in a voltaic cell to produce electricity, and we use electricity to do the chemical work of electro-plating. We use light to bring about chemical changes in photography, and in the majority of the chemical experiments that we shall perform in the laboratory, heat will be used to start the action or to carry it to completion.

3. *Chemistry is vital to all industry.* The garage and the laundry are small laboratories where chemistry may be applied. In the kitchen the cook uses practical chemistry. This science teaches her why soda and sour milk will make palatable biscuits or pancakes; it will also teach her why soda and sweet milk make biscuits that are yellow and bitter. Our agricultural colleges study the applications of chemistry to soils and fertilizers, and pass their knowledge on to the farmer. The clothing which we use to protect our bodies is sponged, cleaned, or even fabricated by means of chemistry, while the beautiful colors with which textiles are dyed are the fruits of long hours of patient research by the color chemist. (See Fig. 1.)

The chemist is constantly discovering new and better methods of manufacture. He searches for "contact agents" which by their mere presence speed up chemical processes and thus save time and money. He finds new uses for the by-products which are formed during manufacturing operations. The chemist makes our drugs, dyes, medicines, steel, glass, cement, pottery, and hundreds of other useful products. (See Fig. 2.)

4. *Chemistry may be a "hobby" or a life work.* The large number of chemical sets found on the market furnishes proof that chemistry is an interesting "hobby." The boy or girl

who is interested in finding out "why things happen" and "how changes occur" will be fascinated with chemistry. The student who wishes a general education will find in chemistry a subject of broad, cultural value.

Those who make chemistry a life work find that it usually affords a comfortable living. Those who delve deeply into

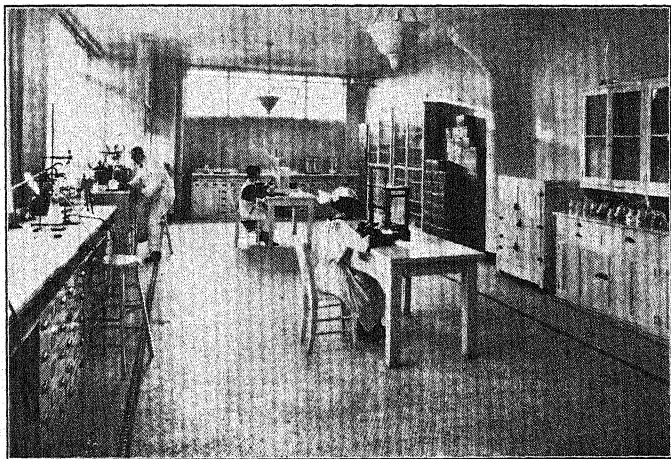


FIG. 1 — A light, well-ventilated, modern laboratory. The tiled floors and white, enameled woodwork make such a laboratory a pleasant place to work.

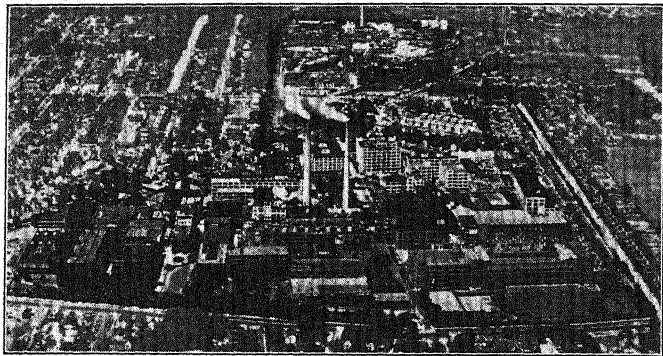
the subject may eventually have the satisfaction of having made some epoch-making discovery.

**2. Alchemy — the Forerunner of Chemistry.** Alchemy bears much the same relationship to chemistry, the youngest of the sciences, that astrology does to astronomy or legend to history. It probably originated in Egypt, and the god Hermes Trismegistus is represented as being its father. Alchemy was probably introduced into Europe by the Arabians.

Geber, who is supposed to have lived in about the eighth century, is reputed to have been the author of several books pertaining to alchemy. His "Summit of Perfection" is

probably the oldest book on the subject in the world. Although it has considerable merit, so much of it is unintelligible to moderns that Dr. Johnson tells us that the word "gibberish" is really derived from the name Geber.

Geber believed that mercury, sulfur, and arsenic were the three elemental chemicals, and that other substances were made up of these three chemicals in different proportions. The alchemists saw mercury dissolve gold, and sulfur pene-



*Courtesy Eastman Kodak Co.*

FIG. 2. — An industrial park, acres in extent. In this plant films are made by a chemical process and coated with chemicals that are sensitive to light. An industry largely dependent upon chemistry.

trate iron like a spirit. Hence their belief that all metals were composed of mercury and sulfur.

During the Dark Ages and the early period of the Revival of Learning in Europe, two different schools of alchemy arose. Many alchemists worked in the monasteries of Europe. The alchemists in one school spent their time in studying the properties of chemicals. Their purpose was to dupe the uninitiated, and they resorted to all kinds of sorcery, magic, and the so-called "Black Arts." The alchemists of the other school sought knowledge for legitimate use. The majority of the alchemists of both schools believed in three things: (1) The transmutation of metals; (2) a universal solvent;

and (3) the elixir of life. Gold was considered the king of metals. It was believed that someone would succeed eventually in finding a "philosopher's stone," and that a piece of lead or other base metal, when rubbed by this stone, would be changed immediately to gold. They spent much time in searching for such a stone. One of the early kings saw an alchemist heat a piece of lacquered gold. When the

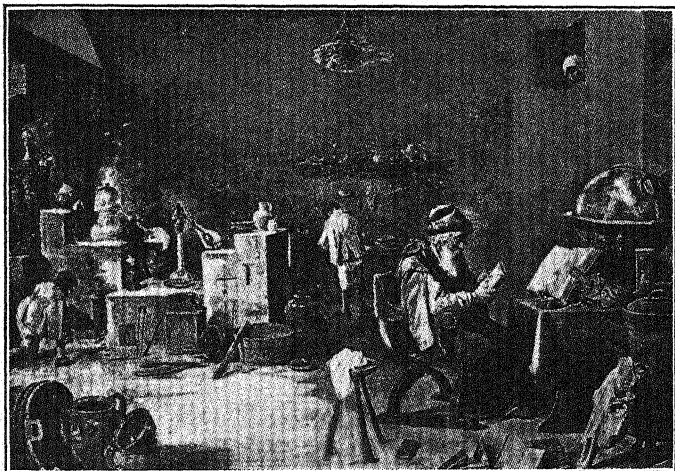


FIG. 3. — A few centuries ago such laboratories were common. Contrast the environment of the old alchemist with that of the workers in the laboratory of Fig. 1.

lacquer burned off, and the gold appeared, the king bought a formula for changing iron to gold. This is an example of the trickery that characterized one group of alchemists. The early alchemists also searched for a fluid that would dissolve gold. They believed that such a fluid would prove to be a universal solvent and that it would also be an elixir of life. The story was told of an old man who turned up a vial of yellow liquid when plowing in Sicily. When he drank the liquid, his youth was restored.

Such beliefs seem foolish to us, but it is easy to understand how they influenced ignorant persons and caused them to believe in witchcraft, sorcery, and charms that persist even today. Dr. J. O. Frank at the Wisconsin State Teachers College has a list of some 1800 things about which citizens of the United States are superstitious. From our study of history, we recall that Ponce de Leon, when an old man, came to America seeking for the "Fountain of Youth."

The other school of alchemists studied the nature of chemicals from a practical point of view. Figure 3 shows a typical laboratory used by the alchemists. They made considerable progress and learned how to prepare many chemical substances and to purify them. They were sincere in their efforts, but they failed to classify their knowledge. Such men as Priestley, Lavoisier, and Scheele organized the jumbled facts that the alchemists had learned, and the science of chemistry was born at about the same time that the thirteen colonies declared their independence and founded a new nation. Chemistry as a science and the United States of America as a nation are of about the same age.

## B. MATTER AND ENERGY

**3. What Is Matter?** All sciences deal with a study of matter, and chemistry is no exception. Everything with which we come into contact is called matter. It may be defined as anything that occupies space or takes up room. In other words, *matter has volume*. We detect its presence by the aid of one or more of the senses, as sight, smell, taste, or touch.

All students are familiar with matter in the solid or liquid state, but some persons may question the fact that gases occupy space. If we try to pour water into a bottle through a small opening, we find it difficult or impossible unless there is a second opening through which the air inside the bottle

may escape. (See Fig. 4.) When a tornado topples over buildings or blows down trees, we are conscious that gaseous air is matter. Then, too, we ride on an air cushion in our automobile tires.

**4. Three States of Matter.** There are three states of matter: solid, liquid, and gaseous. A block of wood placed on the table maintains its form and its volume. It does not need lateral support to prevent its distortion, because it is a *solid*. Many solids are so rigid that they may be subjected to considerable pressure without becoming distorted. *Solids have a definite volume and a definite shape.*

If we pour a quart of water out on the table, it will spread out over the table in all directions. When put into a container, it will take the same shape as the container, but its volume will still be equal to one quart. Thus we see that *liquids have a definite volume, but they take the shape of their container.*

If we pump up a pneumatic tire, the air takes the shape of the tire. When a blow-out occurs, the air expands. Gases expand easily, and they are readily compressed. *Gases have neither a definite shape nor a definite volume.* In fact, gases change their volume so easily when the temperature or the pressure changes that it is necessary to have a *standard temperature and pressure* at which gas volumes are measured. *The standard temperature used for measuring gases is 0° C.* A table that shows how to compare Fahrenheit and Centigrade thermometer scales is given in the Appendix. *The standard pressure used for measuring gases is the pressure which the air exerts at sea level.* It is equal to the pressure exerted by a column of mercury 760 mm. high, or about 30

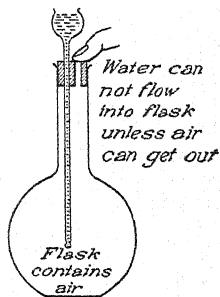


FIG. 4. — Two things cannot occupy the same place at the same time. This is an example of the law of impenetrability.



inches. It is also equal to about 14.7 pounds per square inch. If we speak of one quart of gas, we may specify that it measures one quart when the temperature of the gas is  $0^{\circ}\text{C.}$ , and the pressure it sustains is equal to 760 mm. of mercury. The abbreviation S.T.P. is used to indicate standard temperature and pressure. Both liquids and gases are called *fluids*, from the Latin word *fluere*, which means "to flow."

5. **Measurement of Matter.** Two systems of measurement are in common use, the English system and the Metric system. The English system is probably well enough known so that it need not be discussed here.

The Metric system is a decimal system. It is used in all civilized countries except Great Britain and the United

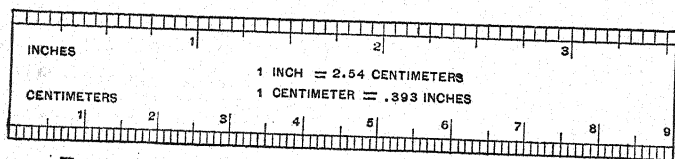


Fig. 5. — Comparison of Metric and English units of length.

States, and it is used for scientific work in *all* countries. The unit of length is the *meter*. It is divided into tenths, or *deci*-meters; into hundredths, or *centi*-meters; and into thousandths, or *milli*-meters. Ten meters make 1 *deka*-meter; 100 meters, 1 *hekto*-meter; and 1000 meters, 1 *kilo*-meter. Arranged in tabular form:

10 millimeters	(mm.)	make 1 centimeter	(cm.).
10 centimeters	(cm.)	make 1 decimeter	(dm.).
10 decimeters	(dm.)	make 1 meter	(m.).
10 meters	(m.)	make 1 dekameter	(Dm.).
10 dekameters	(Dm.)	make 1 hektometer	(Hm.).
10 hektometers	(Hm.)	make 1 kilometer	(Km.).

The meter equals 39.37 inches; 1 inch equals 2.54 centimeters. (See Fig. 5.)



The metric unit of capacity is the *liter*. The same prefixes are used as in the table of lengths. A cubical box 10 centimeters on a side holds 1 liter; thus it is equivalent to 1000 cubic centimeters, or 1 cubic decimeter. It is slightly smaller than the *dry* quart and a little larger than the *liquid* quart. (See Fig. 6.)

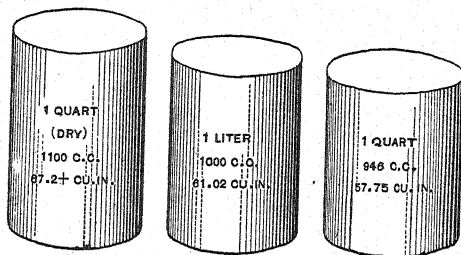


FIG. 6. — Relative sizes of the *dry* quart, the liter, and the *liquid* quart.

The metric unit of weight is the *gram*. The same prefixes are used as in the table of lengths. *One liter* of distilled water, at  $4^{\circ}\text{C.}$ , weighs 1 kilogram. Therefore 1 cubic centimeter of water weighs 1 gram. The student will do well to remember the following:

1. An ordinary nickel weighs almost exactly 5 grams.
2. The liter equals 1000 c.c., and one c.c. of water weighs 1 gram.
3. One meter equals 39.37 inches.
4. One kilogram equals a little more than 2.2 lb. (See Fig. 7.)

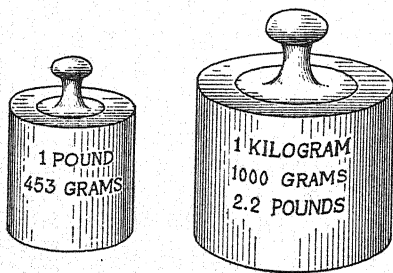


FIG. 7. — The kilogram is more than twice as heavy as the pound.

## 6. What Is Energy?

In order to bring about any change in the condition of matter, energy is needed. It also requires some form of energy to produce motion in matter. In turn, changes in matter itself may liberate various forms of energy. We must heat a piece of wood in order to make it burn, but it gives out heat as the

wood continues to burn. *Energy may be defined as the capacity for doing work.*

**7. Kinds of Energy.** There are several kinds of energy: *mechanical energy; heat energy; electrical energy; light energy; and chemical energy.* For doing chemical work all the above-named kinds of energy are used extensively. It is possible to *convert* or *transform* one kind of energy into a different form. For example, one may use the heat energy from burning coal to produce steam; the steam may be used in a steam engine to produce mechanical energy; such energy may be used to run a dynamo to produce electricity; the electrical energy from the dynamo may in turn be converted into heat energy, into light energy, or into mechanical energy as used to drive motors.

**8. Conservation of Energy.** In the earth's treasure house we find stored or *potential* energy in coal and petroleum. In their formation, energy from the sun was utilized. Although it is impossible to *destroy energy*, yet as these natural stores of fuel are burned, we utilize the heat energy produced, but we cannot supply beds of coal or lakes of oil to take their place. The *fact* that energy cannot be destroyed is known as the **LAW OF THE CONSERVATION OF ENERGY**. The fact that man cannot create energy is just as important, and it serves to emphasize the need for conservation of those natural resources that cannot be replaced.

Energy in motion is called *kinetic* energy, from the Greek word *kinein*, which means "to move." The winds, tides, ocean waves, and running water are common examples of kinetic energy.

### SUMMARY

Chemistry is a cultural subject, because it answers many important questions. It is closely related to the other sciences. It is vital in all types of industrial operations. It may become a fascinating hobby for one's recreation, or a life work that offers interesting possibilities.

Alchemy had its birthplace in Egypt. It was introduced into Europe by the Arabians. Two schools of alchemy arose in Europe: The alchemists of one school spent their time in seeking for knowledge for practical purposes. The alchemists of the other school resorted to trickery, sorcery, and the practice of the "Black Arts."

Matter is anything that occupies space. Many different substances may exist in either the solid, liquid, or the gaseous state of matter. The state depends almost entirely upon the temperature.

The Metric system is used extensively in scientific work. The *meter* is the unit of length; the *liter*, the unit of capacity; and the *gram*, the unit of weight. The gram, the liter, and the cubic centimeter will be used very often in the laboratory.

The student should remember that: (1) One c.c. of water weighs one gram; (2) the liter equals 1000 c.c.; (3) one kilogram equals a little more than 2.2 lb.; and (4) the gram is so small that a five-cent piece weighs about 5 grams.

Energy is defined as the capacity for doing work. *Mechanical, heat, light, and chemical* energy may be converted from one form into another, but *it is impossible to create or to destroy energy*. This statement is called the LAW OF THE CONSERVATION OF ENERGY. The energy of the water in Lake Erie is largely *potential*, but it becomes *kinetic* as the water flows over Niagara Falls.

### PROBLEMS

1. Find the number of grams in one pound. Find your weight in kilograms.
2. Reduce your height to meters. Find the value of 10 Km. in miles.
3. What must be the dimensions in decimeters of a cubical box whose capacity is one liter? How many cubic centimeters are there in 22.4 liters? How many times can a 100-c.c. beaker be filled from a flask that holds one liter?
4. A pneumatic trough is 30 cm. long, 2 dm. wide, and 80 mm. deep. What is its capacity in c.c.? In liters?

5. A bottle holds 1650 c.c. How many liters of water does it hold? How many grams? How many kilograms?
6. A test tube 6 in. long has an internal diameter of  $\frac{3}{4}$  in. How many c.c. does it hold?
7. Measure the length of this page in inches. Reduce this measurement to centimeters.

### SUPPLEMENTARY PROJECT

Prepare a report on the life and work of one or more of the following: Paracelsus, Van Helmont, Francis Bacon.

Reference: Any good encyclopedia.

## CHAPTER 2

### ELEMENTS — MIXTURES — COMPOUNDS

#### Vocabulary

**Element.** A substance that is the limit of chemical analysis.

**Mixture.** A complex of two or more substances in no fixed proportion.

**Compound.** A substance consisting of two or more elements in a definite proportion by weight.

**Chemical affinity.** The attraction between atoms.

**Analysis.** (*ana*, "up"; *luain*, "to loose.") The decomposition or separation of a compound into its elements.

**Atom.** The smallest part of an element that can enter into combination with other elements.

9. **Introductory.** If we examine a piece of granite, we find that it is made up of several different substances. It is a *mixture* of three different minerals. If we examine carefully a piece of copper and a crystal of sugar both *appear* to be simple substances. All efforts to decompose copper have resulted in failure, and the chemist regards copper as an *element*. In the case of sugar, its appearance is deceitful. In other words, we cannot rely upon appearances in our attempts to determine which substances are elements and which are compounds. It is possible to decompose sugar into simpler substances. When it is charred, the carbon in the sugar becomes visible, and the chemist finds by analysis that sugar also contains hydrogen and oxygen. Sugar is a *compound*. Since chemistry is the science that deals with elements and compounds and the chemical changes that compounds undergo, the beginner must acquire a definite concept of each of these three terms, namely: *element*, *mixture*, and *compound*.

**10. The Element Is the Limit of Analysis.** The student of English may analyze a complex or a compound sentence in order to find the elements of which it is composed. In a similar manner, the chemist may start with a complex substance, or with a chemical compound, and separate or decompose it into simpler substances by analysis. If he passes an electric current through water containing a little acid, he finds that the water is decomposed into two gases, hydrogen and oxygen. We call hydrogen and oxygen elements, *because all attempts to split them up into simpler substances have resulted in failure*. The element is considered as the limit of chemical analysis.

About the beginning of the twentieth century, chemists learned that some of the so-called elements do explode spontaneously. But since no chemist can bring about such a disintegration of the element by any chemical action, or check it when it has started, the *element* is considered in all analytical work as the chemist's unit.

It is quite impossible to prove that any given substance is an element. We know that no one has yet succeeded in decomposing iron, oxygen, copper, or gold into anything simpler, but we cannot prove that someone may not succeed in doing so in the future by some as yet untried method. It is considered doubtful, but not impossible. The early Greeks considered fire, earth, air, and water as elements. Research work has proved that they were wrong in all cases. Air and earth are mixtures of several different substances, and water is a compound. It was considered an element, however, until 1766 when Henry Cavendish recognized hydrogen as an element and found that it would combine or unite with oxygen to form water. Thus the chemist finds that he can make oxygen and hydrogen combine to form water, or he can decompose water and produce hydrogen and oxygen. Hydrogen, from the Greek words *hudor*, "water," and *genes*, "producing," was named by the French chemist Lavoisier.

**11. The Number of Elements.** At the present time ninety-two substances are known that chemists have good reason to consider elements. New elements have been discovered from time to time, but there are good reasons for believing that no more elements will be discovered. Careful study has led chemists to believe that there are only ninety-two elements of which the earth's crust is composed. Only about thirty elements are well known. The names of such elements as dysprosium and ytterbium, for example, are not familiar even to well-educated persons. Lanthanum is not a household word. The student should compare the list of fairly common elements printed on the inside of the front cover with the complete list of elements given on the inside of the back cover of this book.

**12. Abundance and Distribution of Elements.** Several elements are present in the air, but nitrogen and oxygen comprise about 99% of it. We have learned that water is composed of hydrogen and oxygen. F. W. Clarke, of the United States Geological Survey, has estimated the abundance of eight elements found in air and water and in the earth's crust (near the surface only) as follows:

Oxygen . . . . .	49.9%	Calcium . . . . .	3.4%
Silicon . . . . .	26.0	Sodium . . . . .	2.3
Aluminum . . . . .	7.9	Potassium . . . . .	2.3
Iron . . . . .	4.4	Magnesium . . . . .	2.1

Thus we see that oxygen comprises nearly one-half of the earth as we know it, and silicon, which is found in sand and clay, comprises more than one-fourth. We must consider the above figures as an estimate only, and keep in mind that nothing is known of the composition of the earth's crust below the depth of a few miles.

**13. How Do Metals Differ from Non-metals?** Some elements have a luster like steel or silver. They reflect light readily. They conduct heat and electricity remarkably well. Some of them can be drawn into wire or hammered into

sheets. Elements that have such properties are called *metals*. Copper, iron, zinc, tin, lead, mercury, silver, and gold are examples of metallic elements. To the chemist, metals are known as *base-formers*, because many of them unite with oxygen and hydrogen to form compounds that are called *bases*. Some bases have the properties of an *alkali*, quite the opposite to the properties of an *acid*.

Sulfur is a typical *non-metal*. It is a poor conductor of heat and electricity. It has a vitreous or glassy luster. It is an *acid-forming* element. Other non-metals that are solid at room temperature include carbon, iodine, and phosphorus. Such gaseous elements as oxygen, nitrogen, and chlorine are also non-metals.

**14. How Are Elements Named?** Some elements are named from the country in which they were discovered, some from the source of the element, and others from some peculiar property of the element. For example, scandium was found in Scandinavia. Aluminum was at one time obtained from alum. Chlorine is named from the Greek word *chloros* because it has a greenish yellow color, and bromine comes from the Greek word *bromos* which means "stench." *Illinium* was discovered by Dr. Hopkins of the University of Illinois (Fig. 8). Dr. Allison of the University of Alabama discovered *alabamine* and *virginium*.

The more recently discovered metallic elements take a Latinized ending "um" or "ium." Sodium, calcium, virginium, radium, and aluminum are examples. The only non-metal that has the ending "ium" is helium. It was discovered in the sun and believed to be a metal. When found later in our atmosphere, it proved to be a non-metal. The element takes its name from the Greek word *helios* which means "sun." The metals which were known to the ancients have no distinctive endings. Iron, tin, lead, copper, silver, mercury, and gold are examples.

A list of non-metals includes nitrogen, oxygen, carbon,



chlorine, iodine, and alabamine. The ending given to the names of most non-metals is "en," "on," or "ine."

**15. What Is Meant by a Symbol?** The alchemists used symbols to represent elements and compounds. Some of them were based upon astronomical symbols; some had their origin in mythology; and others were mystical. They varied from time to time and many different symbols for the same element were used in one manuscript. (See Fig. 8a.)

Berzelius, a Swedish chemist, was the first to use letter abbreviations for the elements. He found it easier than drawing figures, and it is certainly much simpler. He decided to use the first letter of the element as its symbol. For example, the letter O represents oxygen and the letter H represents hydrogen.

Since there are ninety-two elements and only twenty-six letters, several elements begin with the same letter. Berzelius suggested using the second letter of the element with the first in such cases, or using some other letter whose sound is conspicuous when the name is pronounced. For example, the symbol for carbon is C; for calcium, Ca; for chlorine, Cl; for chromium, Cr; and for cobalt, Co. The first letter of a symbol is always a capital, but the second letter of a symbol is never capitalized.



Photo by Underwood and Underwood

FIG. 8. — Dr. B. S. Hopkins, of the University of Illinois, is the first American who ever discovered an element. He named the element *illinium*.

In several cases, the symbol is derived from the Latin name of the element. For example, the symbol for iron is Fe, which comes from the Latin word *ferrum*. Pb from the Latin word *plumbum* is the symbol for lead; the symbol Ag,

which represents silver, comes from the Latin word *argentum*; and Na from the Latin word *natrium* is the symbol for sodium. The table inside the front cover gives the names and symbols of several elements.

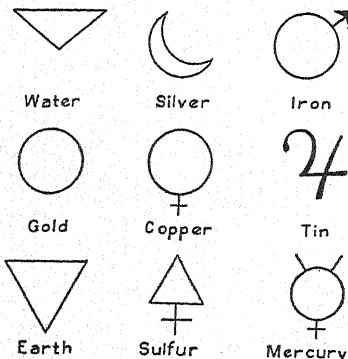


FIG. 8a. — Symbols used by alchemists.

But a symbol in chemistry is *more than an abbreviation*. When we use the symbol O to represent oxygen, *it means one atom of oxygen*. The atom is the chemist's unit.

It is the smallest particle of an element that can enter into combination with other elements. Just as a mason uses different kinds of bricks to build houses, so the chemist uses different kinds of atoms to build chemical compounds. A mason may cut a brick into two or more parts, however, but the chemist cannot break an atom into parts. To the chemist, then, the symbol O means one atom of oxygen, indivisible and of definite weight. The symbol H represents one atom of hydrogen.

**16. How Mixtures Differ from Compounds.** When matter is made up of two or more elements, they may be mechanically mixed, or they may be chemically combined. (See Fig. 9.) It is very important for the beginner to understand the difference between a *mixture* and a *compound*. Suppose we perform the following experiment: To some iron filings on a piece of paper let us add some powdered sulfur. When we stir them together, there is no apparent action. No light

is given off, no heat is liberated, and there is no evidence that electricity is produced. The two elements may be *mixed* in any proportion, equal parts, two to one, or one to one hundred. Next we may pass a magnet over the mixture. The iron filings will

cling to the magnet, but the sulfur is not attracted. We may dissolve the iron filings in hydrochloric acid, but the

sulfur will not dissolve. We may consider this behavior as typical of the properties of a *mixture*.

Next let us put this mixture into a test tube and heat it until the contents begin to glow. Even after we remove the tube from the flame, the action continues, and the whole mass becomes red hot. *Both heat and light were produced during the chemical action that caused the sulfur to unite chemically with the iron and form a compound.* Attraction between atoms that causes them to combine and form *compounds* in this manner is called *chemical affinity*. It is typical of the formation of some other compounds.

Let us break the tube and examine the product. It does not resemble either the iron or the sulfur. The iron cannot be removed by a magnet. The sulfur cannot be picked out mechanically. If we took the product to a chemist to be analyzed, he would find that it is made up of 7 parts by weight of iron to 4 parts by weight of sulfur. A compound is always made up of the same elements in a definite composition by weight. If we had started with a different ratio, any excess of either element would have been left uncombined. Eight parts of iron unite with 4 parts of sulphur, but 1 part of iron is wasted. The several differences between a mixture and a compound are summarized in the following table:



FIG. 9. — Mixtures and compounds are made up of elements. In compounds the elements are united chemically.

## MIXTURE

*In a mixture the constituents may be in any proportion.*

*In preparing a mixture, there is no evidence of any chemical action, such as the evolution of heat, light, or electricity. No gas is set free.*

*A mixture may often be separated by mechanical means.*

## COMPOUND

*A compound always has a definite composition by weight.*

*In the preparation of a compound, some evidence of chemical action is apparent. Heat or light may be emitted or absorbed, an electric current may be produced, or a gas liberated.*

*The constituents of a compound can be isolated by chemical means only.*

Air is a mixture; its composition varies somewhat in different localities. Hash is a mixture; one can identify or pick out the particles of meat or potato. Other examples of mixtures are baking powder, granite, salads, and the different kinds of soils. It is possible to have a mixture consist of two or more elements, of two or more compounds, or of elements and compounds.

Some of our dictionaries contain almost a half million words, all formed from 26 letters. Imagine the number of possible compounds that could be formed from 92 elements. But just as some letters do not combine to form words, so some elements do not combine with others to form compounds. There are enough such combinations, however, to form *several hundred thousand compounds*. Water, table salt, sugar, marble, alcohol, baking soda, glycerine, nitric acid, and sulfuric acid are examples of compounds used by chemists.

**17. Law of Definite Proportions.** We know that the ingredients in a mixture may be in any proportion, but that the constituents of a compound are always present in a definite ratio. This characteristic nature of compounds was observed by an English schoolmaster, John Dalton, who formulated the **LAW OF DEFINITE PROPORTIONS**: *Every compound has a definite composition by weight.* (See Fig. 10.)

*Symbols* are used to represent elements. To the chemist the symbol stands for *one atom* of the element.

A material made up of two or more elements is either a *mixture* or a *compound*. If the elements are chemically combined and their proportion is definite, the substance is a *compound*. In a *mixture* the ingredients may be present in any proportion.

The Law of Definite Proportions was formulated by John Dalton. It may be stated as follows: *Every compound has a definite composition by weight.*

## QUESTIONS

1. Name five elements; six compounds; four mixtures.
2. Name the six most abundant elements.
3. If you were given a mixture of sand and sugar, how could you separate them?
4. How could you separate the iron from a mixture of iron filings and sulfur?
5. Is it possible to separate the iron from the sulfur in the compound iron sulfide? If so, how? (Class discussion.)
6. State some of the characteristic properties of (a) gasoline, (b) alcohol, (c) gold, (d) copper, (e) silver.
7. How would you distinguish between alcohol and gasoline? How would you tell gold from copper? Salt from sugar?
8. Why has the concept of the element changed from time to time?
9. Read over the list of elements and symbols printed on the inside of the front cover. Close the book and write from memory the names of ten elements with their symbols.
10. Is it correct to say that the physical properties of a substance depend upon its behavior when alone, and its chemical properties upon its behavior or conduct with other substances?

## CHAPTER 3

# NATURE OF MATTER AND ITS CHANGES

### Vocabulary

**Precipitate.** A substance, usually a solid, separated from a solution as a result of some physical or chemical change.

**Molecule.** The smallest particle of matter that can exist and retain the properties of the mass.

**Electron.** The smallest particle of matter. A negatively charged particle of matter.

**Synthesis.** Putting together elements to form a compound.

**Substitution.** Replacing one element in a compound by means of another element.

**Metathesis.** An interchange of the elements in two different compounds.

**Exothermic.** Liberating heat as the reaction occurs.

**Endothermic.** Absorbing heat as the reaction occurs.

**Electrolysis.** Decomposition of a compound by means of an electric current.

### A. NATURE OF MATTER

**20. Nature of Matter.** If we open a gas jet, the odor of gas may shortly be detected in the room. No particles of gas can be seen in the air, even with the best microscope, yet our olfactory nerves tell us that they have been stimulated in some manner. When salt has been dissolved in water, no microscope is powerful enough to detect its presence, but our sense of taste tells us that the solution contains salt. Many similar experiments may be performed, and all of them serve to convince us that all matter is made up of exceedingly small particles, called *molecules*. They are so small that it would probably take one million molecules laid side by side to make a line one millimeter long. The best estimates show that a liter (approximately one quart) of gas at standard tempera-

ture and pressure contains about  $27 \times 10^{21}$  molecules. If the student writes the figure 27 with 21 ciphers following it, he may have a better concept of the extremely minute size of the molecule. An average adult, by deep breathing, can inhale about four times that number of molecules at a single inhalation. It is estimated that if a drop of water were magnified until it became as large as the earth, its molecules, if magnified correspondingly, would be about the size of baseballs.

From the preceding paragraph, one would infer that the molecules of gases must be closely crowded. Relatively, they are not even near neighbors. When we pump up an automobile tire to a pressure of sixty pounds per sq. in., we are merely crowding more than four times as many molecules of air into the tire. This proves that the space between adjacent molecules of gases is much greater than the space occupied by the molecules themselves. *The molecule is the physicist's unit.*

Small as the molecules are, they are believed to be made up of still smaller particles called *atoms*. *The atom is the chemist's unit* from which he builds compounds. It is indivisible by either physical or chemical means.

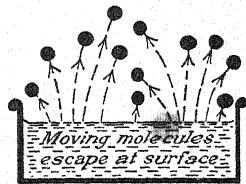


FIG. 11. — During evaporation molecules escape at the surface of the liquid.

**21. What Is the Kinetic Theory of Matter?** Several facts show quite conclusively that the molecules of matter are always in motion. The fact that liquids evaporate is one evidence of such motion. (See Fig. 11.) The decided odor of camphor, musk, and naphthalene (moth balls) is proof that the molecules of solids are in motion. Gas rushes out of a stop-cock when it is opened, and both gases and liquids intermingle through a porous membrane. The kinetic (*kinein*, "to move") theory assumes that the molecules of matter are in constant motion.

When water is heated, it evaporates faster. *An increase in temperature increases the rate at which the molecules move.* The melting of solids when they are heated is further proof of the increase in the rate of molecular motion with an increase of temperature.

22. What Is the Electron Theory? We have learned that the atom is indivisible "by chemical means." There is considerable evidence, however, that some atoms explode

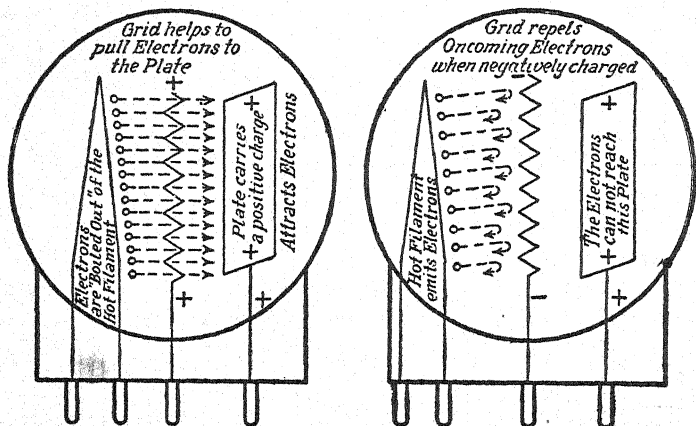


FIG. 12. — The positively charged plate attracts the negatively charged electrons. When the grid is negatively charged, it repels the electrons.

spontaneously. The *electron theory* assumes that the atoms of all matter consist of both positive and negative electricity. Each atom has a nucleus of positively charged particles called *protons*. While there are some negatively charged particles, or *electrons*, in the *nucleus*, yet it always has an *excess of protons*. Figure 12 shows how electrons travel across an audion tube.

According to the theory proposed by Lewis and Langmuir, the electrons surrounding the nucleus are arranged in concentric shells. Figure 13 shows the configurations of some of the lighter atoms. The electrons are assumed to occupy



positions at the corners of an imaginary cube, in the center of which there is the positively charged nucleus.

The theory proposed by Dr. Bohr pictures the electrons as surrounding the nucleus, but revolving around it in a manner

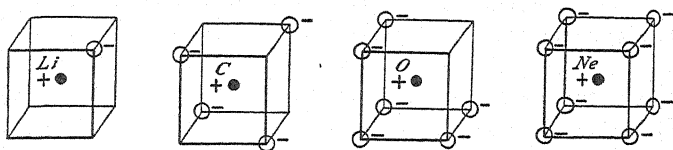


FIG. 13. — The concept of the atoms of lithium, carbon, oxygen, and neon as shown by the Lewis-Langmuir theory.

similar to the revolution of the planets around the sun. Hence the electrons outside the nucleus are called *planetary electrons*. The hydrogen atom has only one planetary electron, but some of the heavy atoms may have many more, the heaviest atom having ninety-two. In the normal un-

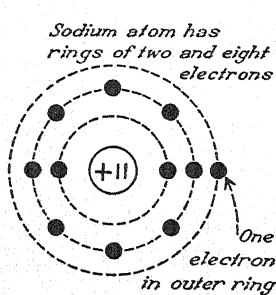


FIG. 14. — The sodium atom as represented by the Bohr theory.

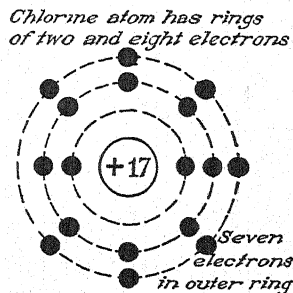


FIG. 15. — The chlorine atom.

combined atom, the sum of the negative charges on the planetary or external electrons exactly equals the charge on the positive nucleus. Such an atom is neutral; it shows no signs of electrification.

The sodium atom of Fig. 14 has a single electron in the outer ring. It may lose this electron and acquire a positive

charge of electricity. The symbol for the sodium atom is  $\text{Na}$ ; when it loses its outer electron, it acquires a plus charge ( $\text{Na}^+$ ). Figure 15 represents a chlorine atom which has seven electrons in its outer ring. To complete a ring of eight electrons, it may borrow one electron from the sodium atom. Then it acquires a negative charge, and we may represent the symbol  $\text{Cl}$  for chlorine as  $\text{Cl}^-$ . But the student of physics knows that two particles that carry opposite charges of electricity *attract* one another. Hence the positively charged sodium atom ( $\text{Na}^+$ ) unites with the negatively charged

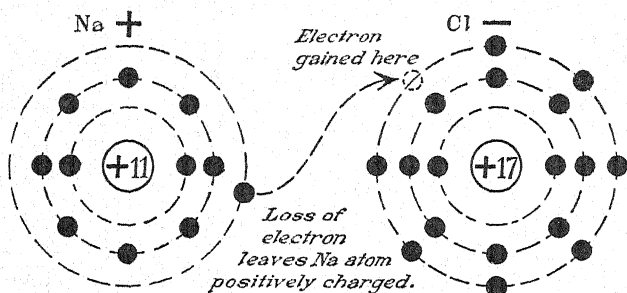


FIG. 16. — The positively charged sodium atom unites chemically with the negatively charged chlorine atom.

chlorine atom ( $\text{Cl}^-$ ) to form a molecule of sodium chloride,  $\text{NaCl}$ , or common table salt. (See Fig. 16.) What is called chemical affinity, or the attraction between atoms, is probably due to the attraction between atoms charged with electricity of opposite sign.

**23. Formulas of Compounds.** In the preceding section, we learned that one sodium and one chlorine atom combine to form a molecule of sodium chloride. A formula is used by chemists to show of what elements a compound is composed. The formula for sodium chloride is  $\text{NaCl}$ . It represents *one* molecule of sodium chloride, and shows that the molecule is made up of one atom of sodium and one atom of

chlorine. In a similar manner, the expression  $2\text{NaCl}$  represents *two* molecules of sodium chloride, each containing one atom of sodium and one atom of chlorine. The formula for water is  $\text{H}_2\text{O}$ . It represents one molecule of water, and shows that it contains *two atoms* of hydrogen and *one atom* of oxygen. A small subscript figure written after a symbol shows the number of atoms of the element represented by that symbol there are in one molecule of the substance. The formula  $\text{H}_2\text{O}$  is read H-two O. The formula for sulfuric acid is  $\text{H}_2\text{SO}_4$ ; it is read as follows: H-two SO-four. Each molecule of the compound sulfuric acid contains two atoms of hydrogen, one atom of sulfur, and four atoms of oxygen.

## B. CHANGES IN MATTER

**24. Physical and Chemical Changes.** Ice melts, water changes to steam, liquids freeze, glass breaks, and sugar dissolves in water. We may magnetize a piece of steel or we may pass a current through a copper wire. In all these cases the matter undergoes some change. Its form may be different or it may change its state, but in no case has the substance lost its identity. Its *molecule*, the physicist's unit, has not been broken up. *The change in all these cases is physical. Physics is defined as the science that deals with physical changes in matter. A change in matter that does not change the characteristic properties of a substance, or destroy its identity, is a physical change.*

Wood burns, iron rusts, milk sours, plants decay, and acids interact with metals. In each of these cases, the identity of the original substance or substances is lost, and new substances with new properties are produced. *These changes are chemical.* In some cases the original molecule is torn down and simpler molecules are formed. In other cases, two elements unite to form a compound. It often happens, too, that atoms rearrange themselves in the molecule, thus forming a new substance with decidedly different properties.

*Chemistry is defined as the science that deals with chemical changes; it also includes a study of elements and compounds.*

**25. How Can One Bring About a Chemical Change?** The chemist has at his disposal several agents that can be used to start a chemical change or to accelerate it. The following are most commonly used: —

a. *Heat.* If we apply a lighted match to a piece of paper, the paper begins to burn. The heat from the burning match starts the chemical change. We kindle the match head by rubbing it over a rough surface to warm it by friction. All are familiar with the chemical changes caused by heat during the baking of bread or the cooking of other foods. Generally, increasing the temperature accelerates such a chemical change. For that reason, a food placed in boiling water at  $100^{\circ}\text{C}$ . will cook in half the time that it does in a fireless cooker at  $90^{\circ}\text{C}$ . An increase in temperature of  $10^{\circ}\text{C}$ . reduces the time needed for a chemical reaction to about one half.

b. *Light.* If we open the shutter of our camera for only a fraction of a second, the light enters and starts a chemical change in the film or plate. The colors of some rugs, draperies, and clothing change or fade in sunlight. Some chemicals are kept in dark-colored bottles to prevent the action of light upon them. The green leaves of plants are capable of making starch out of the raw materials obtained from the air and the soil, provided they are exposed to sunlight. If a plant is kept in the dark, its green color disappears; it can no longer make starch.

c. *Electricity.* If one passes a current of electricity through water that contains a little acid in solution, hydrogen is liberated at one of the electrodes and oxygen at the other. Many compounds, if melted or if dissolved in water, can be decomposed into their elements by passing an electric current through the molten mass, or through the water solution. Electricity is used commercially to produce chemical changes

in the refining of metals, in electroplating, in electrotyping, or in charging storage batteries.

d. *Solution in water.* Baking powder is a mixture of compounds. No action between them occurs as long as the powder is kept *dry*, but chemical action begins at once when water is added. Many chemicals that do not react in the dry state begin to interact when dissolved in water.

**26. What Are Some Evidences of Chemical Action?** It is an interesting fact that some of the forms of energy that cause chemical changes are also evident during the change. For example, external heat is needed to start the burning of coal, but heat is set free continuously as the coal burns. *A chemical reaction that liberates heat energy as it proceeds is said to be exothermic.*

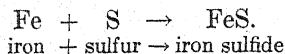
In the burning of coal, *light energy* is also set free. Hence we assume that the evolution of heat energy and light energy is evidence of chemical action. When water is added to baking powder, a gas is set free. This is evidence of chemical action. The mechanical energy produced when dynamite or nitroglycerine explode, as well as the heat and light liberated, is also evidence of chemical action. In a voltaic cell, the negative plate is acted upon chemically, and the chemical energy is transformed into electrical energy.

In some cases, however, heat is absorbed all the time that the chemical action is taking place. In making calcium carbide, the raw materials are heated in the electric furnace during the entire period of its manufacture. A reaction that absorbs heat as it progresses is said to be *endothermic*.

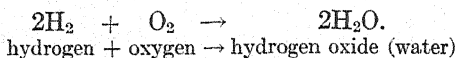
**27. Types of Chemical Change.** We have already learned that the chemist cannot split up atoms, but he may combine them, decompose compounds into atoms, substitute one atom for another in a compound, or interchange atoms between two compounds.

1. *Composition, or synthesis.* When we heated iron filings and sulfur, one iron atom combined with a sulfur atom to

form a molecule of iron sulfide. The chemist uses symbols and formulas to represent such chemical action in either *word equations* or *formula equations*. For example,



In such an equation, the sign "plus" is read "and," and the arrow is read "yields," "gives," "produces," or "forms." Such a reaction is typical of many that are met with in elementary chemistry. In Section 10, we learned that hydrogen and oxygen would combine to form water. The equation follows:



2. *Decomposition, or analysis.* In the apparatus shown in Fig. 17 let us put some water containing a few drops of

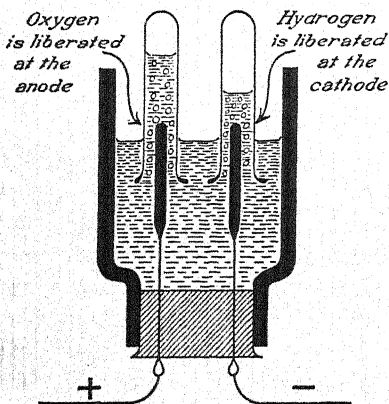
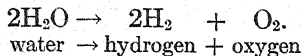


FIG. 17. — As the water is decomposed two volumes of hydrogen are set free at the cathode for every volume of oxygen liberated at the anode.

sulfuric acid. The acid is used to make the water a conductor of electricity. When an electric current is passed through the solution, *electrolysis* occurs, and the water is decomposed into hydrogen and oxygen. The hydrogen collects at the *cathode*, or negative terminal, and the oxygen collects at the *anode*, or positive terminal. These terminals are called *electrodes*.

It is also of interest to observe that the volume of hydrogen set free is just double the volume of oxygen. The equation follows:



Later it will be proved that the molecule of a gaseous element, such as hydrogen or oxygen, contains two atoms. The student will observe that the equation just studied is exactly the reverse of the one given in the preceding para-

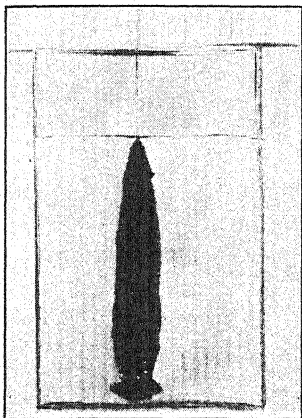


FIG. 18. — The zinc strip goes into solution, displacing the lead which is deposited in the form of crystals.

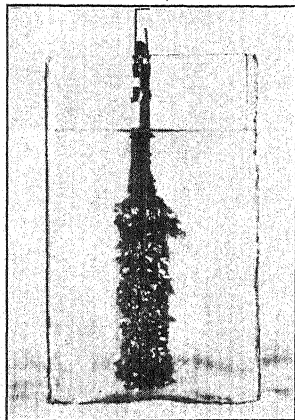
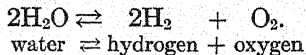


FIG. 19. — The zinc goes into solution, displacing the tin. (Substitution.) Note the tin crystals.

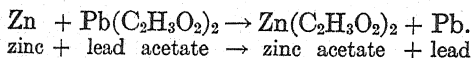
graph. To show that such an equation is reversible, we use a double arrow as follows:



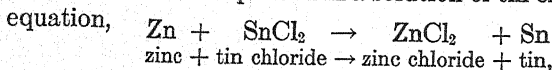
Such an equation does not tell us, however, that we use the electric current to drive the chemical reaction to the right, and that a temperature of about  $800^\circ \text{C.}$  is needed to cause hydrogen and oxygen to unite to form water.

3. *Substitution.* Let us suspend a strip of zinc in a dilute solution of sugar of lead, or lead acetate, and let the apparatus stand for a half hour. (See Fig. 18.) We find that

some of the zinc dissolves and that crystals of lead are deposited on the zinc strip. The equation follows:



We see from the equation that an atom of zinc has substituted itself for an atom of lead. *A chemical reaction in which one element takes the place of another, or is substituted for another, is known as substitution.* Figure 19 represents a zinc rod that has been suspended in a solution of tin chloride. The



shows that zinc substitutes itself for the tin. To use a homely comparison, we may liken the zinc to the boy who goes to a

dance without a partner and then "cuts in" on the partner of another boy. Zinc is a more active metal than either tin or lead.

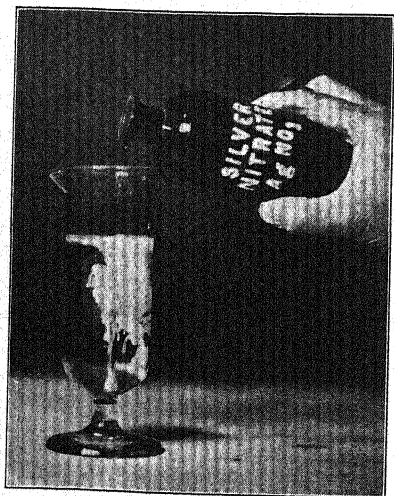


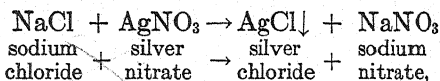
Photo by Wettlin

FIG. 20. — White silver chloride is being precipitated.

4. *Double substitution, or metathesis.* To a solution of common table salt (sodium chloride) let us add a solution of silver nitrate. A white precipitate of solid silver chloride is formed and the precipitate (*thrown down*) sinks to the bottom. (See Fig. 20.) A chemical analysis of the clear

solution would show the presence of sodium nitrate. The equation,





shows that the sodium atom has changed partners with the silver atom. *Such double substitution, or change of partners, is called metathesis.* It is sometimes called double decomposition, on the assumption that both compounds decompose and then an exchange of partners occurs. A downward pointing arrow shows that the compound beside which it is placed is precipitated (thrown out of the solution as a solid).

The great majority of chemical changes are included under the following classes: *composition*, or *synthesis*; *decomposition*, or *analysis*; *substitution*; *double substitution*, or *double decomposition*.

## SUMMARY

Matter is made up of *molecules*, extremely small particles which cannot be seen by the best microscopes. In gases, such molecules are not closely crowded, but the intervening spaces are larger than the spaces occupied by the molecules themselves.

The molecules are composed of *atoms*, which are indivisible by chemical means. The atom is the chemist's unit.

Each atom consists of *protons* and *electrons*. The former is a positively charged particle just equal in weight to the weight of the lightest atom, that of hydrogen. The electron is a negatively charged particle, about  $\frac{1}{1840}$  as heavy as the hydrogen atom.

According to modern theory, the nucleus has an excess of protons, with from 1 to 92 electrons revolving around it in much the same manner that the planets revolve around the sun. The lightest atom has a single electron, and the heaviest atom has ninety-two.

*Formulas* are used by the chemist to represent the composition of the molecule of a substance. The formula shows what atoms are present and the number of each per molecule.

Changes in matter are *physical* or *chemical*; in a physical change the characteristic properties of the substance are not

## 38 NATURE OF MATTER AND ITS CHANGES

lost; in a chemical change a new substance with new properties is formed.

*Heat, light, electricity, and solution in water* aid in producing chemical changes. The various forms of energy — heat, light, and electricity — are often produced as a result of chemical changes.

When heat is liberated during a chemical change the reaction is said to be *exothermic*; when heat is absorbed as the reaction takes place, we have an *endothermic* reaction.

Four types of reactions are common in chemistry: *Composition*, or *synthesis*, is the uniting of two or more elements to form a compound. *Decomposition*, or *analysis*, is the breaking down of a compound into its elements. *Substitution* is a chemical change in which one element takes the place of another. In *metathesis*, two compounds decompose, and their elements interchange to form two new compounds.

### QUESTIONS

1. In your opinion, what causes one atom to substitute itself for another atom?
2. Make a list of as many causes of chemical change as you can.
3. Give several evidences in support of the kinetic theory of matter.
4. What is the significance of a chemical formula, and how does it help the chemist?
5. What are the important differences between physics and chemistry?
6. State whether the following changes are physical or chemical:
  - (a) The burning of wood.
  - (b) The fermentation of sugar.
  - (c) The decay of food.
  - (d) The tarnishing of brass.
  - (e) The evaporation of alcohol.
  - (f) The freezing of water.
  - (g) The souring of milk.
  - (h) The weaving of cotton cloth.
  - (i) The melting of lard.
  - (j) The rusting of iron.
  - (k) The explosion of dynamite.
  - (l) The stretching of a rubber band.

7. Which of the chemical changes listed in the preceding question are exothermic?
8. Which tells a chemist more of what actually happens, a word equation or a formula equation? Explain.
9. The recipes in the older cook books directed one to mix the milk and baking powder, or the sour milk and soda, and then sift in the flour and other dry ingredients. The newer books direct one to mix all the dry ingredients, including the baking powder or the soda, and then add the liquid. Is there a good reason for the latter practice? If so, explain.

## CHAPTER 4

### OXYGEN

#### Vocabulary

**Pneumatic.** Pertaining to gases.

**Catalyst.** A substance used to accelerate a chemical reaction.

**Oxidation.** A process in which oxygen unites with another substance.

**Combustion.** Rapid oxidation in which light and noticeable heat are produced.

**Oxide.** A binary compound containing oxygen and one other element.

**Binary.** A compound that is composed of two elements only.

**Explosion.** Almost instantaneous combustion throughout the entire mass.

**Allotrope** (*allos*, "other"; *tropos*, "turn" or "direction"). Any one of the two or more forms in which an element may exist.

**Spontaneous.** As applied to combustion, starting from its own slow oxidation, without the application of external heat.

**Volatile.** Easily changed from a liquid to a gas or vapor.

**28. Where Oxygen Is Found.** We live at the bottom of an ocean of air. More than 20% of the air is oxygen. The water area of the earth is about three times as big as the land area. Water contains about 88% of oxygen by weight. Oxygen is present in all plant and animal bodies. Clay, sand, and limestone all contain an abundant supply of this element. No element is so abundant as oxygen, and no element is more important.

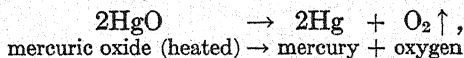
**29. How Oxygen Is Prepared.** As a rule there are several ways of preparing elements or compounds. In the laboratory we select one that is convenient, or one that best illustrates some principle. In commercial work, the chemist must be guided by the cost of raw materials, the expense of plant equipment, and the value of the by-products that are ob-

tained. Common sense would lead us to choose in this case either air, water, or some inexpensive compound that contains much oxygen — a compound which it is not difficult to decompose. Several methods are given here:

1. *Heating mercuric oxide.* (Historical.) Joseph Priestley, a contemporary of George Washington, was an English

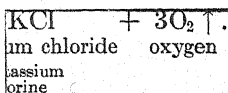
clergyman and scientist. (See Fig. 21.) His religious views and his writings led him into much controversy, and he migrated to America in 1794 and settled at Northumberland, Pennsylvania. He had an inquiring mind, and he was constantly experimenting, especially with gases, which he called "airs." Priestley discovered ammonia, nitrous oxide, and nitric oxide, and invented the pneumatic trough and methods of collecting gases by the displacement of mercury. But his greatest discovery came in 1774, when by means of a lens he focused

the sun's rays upon a red powder known to chemists as mercuric oxide ( $\text{HgO}$ ). This compound contains mercury and oxygen. When it is heated strongly, the oxygen is driven off as a gas, and the metal mercury remains. In the equation,

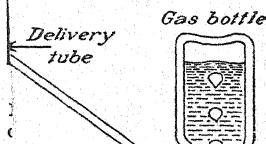


the upward pointing arrow indicates that a gas is produced.

This method of preparing oxygen is too expensive to be of



water, and for that reason it is the method known as water



Priestley was a staunch supporter of the phlogiston theory of combustion. He believed the gas hydrogen to be phlogiston.

any practical value. It is of historic interest only. Priestley did not call the gas which he discovered oxygen, but he described it as "perfect air" or "very active air." He said it had about the same properties as air, but in "greater perfection." He was delighted to find that a candle burned

in this gas with great brilliancy and that a live mouse continued to live in the gas indefinitely. He tells us that he inhaled some of the gas and that his breast felt peculiarly free and light for some time. This gas was named *oxygen* (acid producer) by the French chemist Lavoisier, who believed it to be present in all acids. We know that he was wrong, since some acids do not contain oxygen.

Carl Wilhelm Scheele, a Swedish chemist, working independently of Priestley, discovered oxygen the same year. His

results were not published for five years, and Priestley had by that time been acknowledged the discoverer, but doubtless Scheele should be given equal credit. (See Fig. 22.) Very often it is difficult to give anyone full credit for a discovery or invention, because so many discoveries have been made by different men working independently.

2. *Heating a mixture of manganese dioxide and potassium chlorate.* (Usual laboratory method.) Potassium chlorate is

#### Voca

**Pneumatic.** Pertaining to gase

**Catalyst.** A substance used to

**Oxidation.** A process in which c

**Combustion.** Rapid oxidation are produced.

**Oxide.** A binary compound element.

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**Spontaneous.** As applied to co oxidation, without the applic

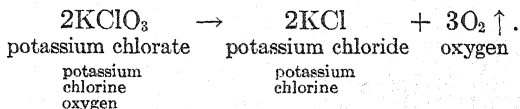
**Volatile.** Easily changed from

#### 28. Where Oxygen Is Fo

an ocean of air. More than

FIG. 22. — Carl Wilhelm Scheele (1742–86). An eminent Swedish chemist, Scheele discovered oxygen, chlorine, baryta, tartaric acid, and an arsenite of copper which is known as *Scheele's green*.

a white, crystalline solid containing potassium, chlorine, and oxygen. Although only a little more than 7% of the weight of mercuric oxide ( $\text{HgO}$ ) is oxygen, yet almost 40% of the weight of potassium chlorate ( $\text{KClO}_3$ ) is oxygen. This compound gives up its oxygen readily when heated, the *decomposition* occurring as shown by the following equation:



The gas is not very soluble in water, and for that reason it can be collected over water by the method known as water

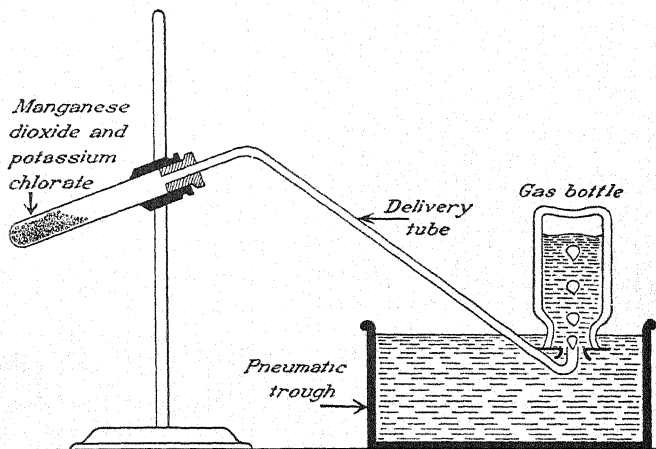


FIG. 23. — Laboratory apparatus for preparing oxygen.

displacement. (See Fig. 23.) The student should compare the formulas for potassium chloride ( $\text{KCl}$ ) and potassium chlorate ( $\text{KClO}_3$ ), and note the difference between them. We do not include the manganese dioxide in the equation, because it takes no part in the chemical reaction. It serves as a "contact agent," a catalyst, or a catalytic agent.

It is possible to prepare oxygen from potassium chlorate without the use of the manganese dioxide. But when the manganese dioxide is present, the potassium chlorate decomposes at a lower temperature and the gas is evolved more evenly and more rapidly. At the end of the reaction, the manganese dioxide is unchanged. What part it plays is

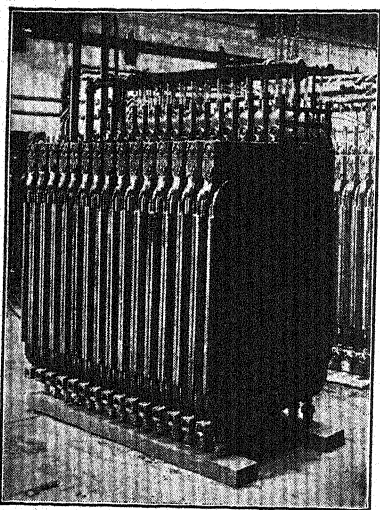


FIG. 24. — Electrolytic cells used for making hydrogen and oxygen.

unknown. We call it a *catalytic agent*, which has been called a term that chemists use "to cover their ignorance." Any substance which by its presence aids in accelerating chemical action without itself being permanently changed is called a *catalyst* or a *catalytic agent*. We shall meet this term frequently, since many chemical reactions proceed so slowly that the success of many manufacturing processes depends upon the use of suitable catalysts. We

may compare the action of a catalytic agent to that of a whip on a horse. It does not help the horse in any way or supply him with energy, but by the slightest contact it makes him go faster. On the other hand, it is sometimes desirable to slow up or to retard some chemical reactions. Some *negative catalysts* are known. For example, acetanilide is added to hydrogen peroxide to keep it from decomposing too rapidly. In a similar way either glue or sawdust will retard the "setting" or hardening of plaster of Paris.

3. *Commercial methods.* Since both air and water are



cheap, and contain an abundant supply of oxygen, the manufacturing chemist naturally turns to them for a commercial supply. Oxygen obtained from either source may be bought in the market.

(1) *From water.* In Section 27 we learned that it is possible to decompose water by passing an electric current through it. A similar process is used commercially, but

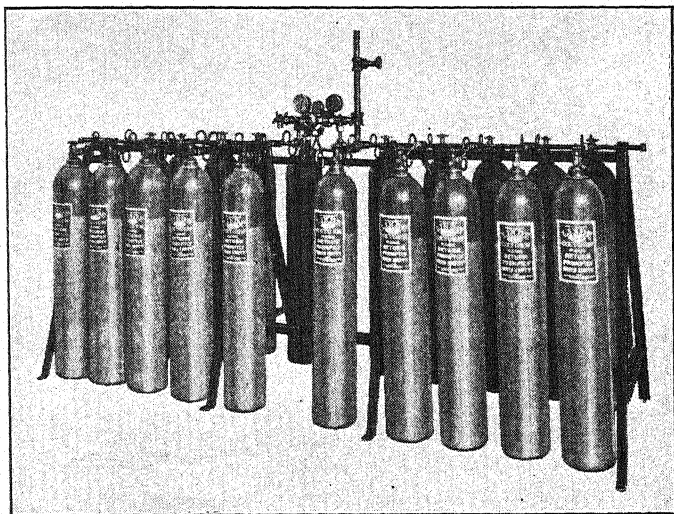


FIG. 25. — Steel cylinders for storing oxygen gas under pressure.

sodium hydroxide instead of sulfuric acid is added to the water to make it a conductor. Figure 24 shows one of the cells in which the oxygen is prepared. This method gives very pure oxygen, but large quantities of electrical energy are needed to decompose the water. Hydrogen is produced as a valuable by-product. The oxygen is forced into steel cylinders under high pressure. This is a general method of preparing gases for market. (See Fig. 25.)

(2) *From liquid air.* Air is a mixture composed largely of

nitrogen and oxygen. By compressing air and cooling it at the same time to a very low temperature, it may be liquefied. Liquid nitrogen has a lower boiling point than liquid oxygen. For that reason the nitrogen will boil away first when the liquid air stands. The oxygen which is left is pure enough for many industrial purposes. The raw material costs nothing, but the machinery used is expensive. Nitrogen, argon, and neon are valuable by-products.

**30. Physical Properties.** Pure oxygen is a colorless, odorless, tasteless gas. It is slightly heavier than air. At standard conditions of temperature and pressure ( $0^{\circ}\text{C}$ . and a pressure of 760 mm. of mercury), 1 liter of oxygen weighs almost 1.43 gm. One liter of air under the same conditions weighs a trifle more than 1.29 gm. Oxygen is slightly soluble in water. One hundred liters of ice water will dissolve nearly five liters of oxygen (S.T.P.). It is interesting to note that 100 liters of water at room temperature can hold only a trifle more than 3 liters of oxygen. Therefore, if water saturated with oxygen gas at  $0^{\circ}\text{C}$ . were warmed to room temperature ( $20^{\circ}\text{C}$ .), about two liters of oxygen would be expelled. This explains why bubbles of gas appear when a glass of cold water is permitted to stand for some time in a warm room. Only a part of the gas bubbles is oxygen, but all gases are less soluble in warm water than in cold. Like all gases, if cooled sufficiently while the pressure upon it is increased, oxygen is converted into a liquid. Liquid oxygen is pale-blue in color.

**31. Chemical Behavior of Oxygen.** Oxygen has been described as an affectionate element: it combines readily with so many other elements. Its most important chemical property is its *activity*. At ordinary temperatures, however, oxygen interacts *slowly* with substances or in some cases not at all. At higher temperatures it reacts *rapidly* with most substances, usually with the evolution of both heat and light.

**32. What Is Oxidation?** Let us scrape the surface of a piece of sheet lead until it is bright and lustrous. In a half

hour we find that it has become dull and tarnished. The oxygen of the air has united slowly with the lead to form this tarnish, which is called lead oxide. In a similar manner the oxygen which we take into our lungs combines with the carbon and the hydrogen which are present in our foods and oxidizes them, forming carbon dioxide ( $\text{CO}_2$ ) and water respectively. (See Section 38.) In both these cases heat is evolved, but there is no light produced. In this way the temperature of our bodies is kept at  $98.6^\circ \text{F}$ . *The process by which oxygen unites with some other substance is called oxidation. The product formed is an oxide.* The decay of wood and vegetable matter, and the rusting of certain metals, are other examples of *slow oxidation*. The effects of *rapid oxidation* are discussed in Section 34.

The oxygen may be furnished by the air, or it may be supplied by some substance which is rich in oxygen and liberates oxygen readily. If a compound gives up its oxygen to a substance readily, we call it a *good oxidizing agent*. Air is an oxidizing agent, but many compounds, such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), nitric acid ( $\text{HNO}_3$ ), and potassium chlorate ( $\text{KClO}_3$ ) are more vigorous oxidizers.

**33. Oxides Are Important Compounds.** When metals combine with oxygen, they form *oxides*. Such metals as tin, iron, copper, zinc, and lead combine with oxygen to form oxides of those metals, either slowly when cold, or more rapidly when heated. Hydrogen unites with oxygen to form water. Carbon unites with oxygen to form either carbon monoxide ( $\text{CO}$ ) or carbon dioxide ( $\text{CO}_2$ ). The prefix "di" is used when there are two atoms of oxygen. Oxides are *binary* compounds. A binary compound contains two elements; the names of such compounds take the ending "ide." For example, an *oxide* consists of oxygen and one other element. A *chloride* contains chlorine and one other element.

**34. What Is Meant by Combustion?** If we hold a piece of magnesium ribbon in the flame of a burner, it will ignite

and burn with a white flame. It unites with oxygen so *rapidly* that noticeable heat and light are both produced. Any chemical action that occurs so rapidly that light and heat are produced is known as *combustion*. (See Fig. 26.) When wood burns, the carbon and hydrogen of the wood unite chemically with the oxygen of the surrounding air. In such cases, *combustion is rapid oxidation in which heat and light are evolved*.

In early times, fire was so mysterious that it was an object

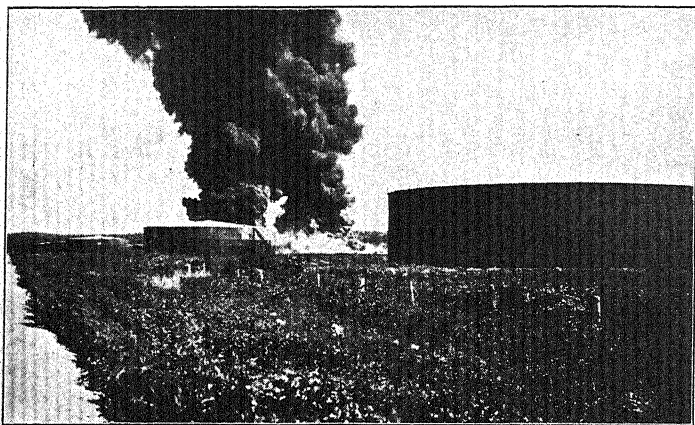


FIG. 26. — A burning oil tank. The combustion is so rapid that only a part of the carbon is oxidized.

of worship in many countries. According to Greek mythology, Prometheus stole fire from the gods, and brought it down to mortals. Many of the alchemists accepted the *phlogiston theory* of combustion. Such elements as carbon and hydrogen were believed to be especially rich in *phlogiston*. When they burned, the phlogiston escaped. When metals burn, the resulting oxides weigh more than the metals weighed originally, but the advocates of the phlogiston theory explained this fact by saying that in some cases

"phlogiston has less than no weight." This absurd theory delayed progress in chemistry for about a century. We would expect that Priestley, after he discovered oxygen, would have learned the true explanation of ordinary burning, but he remained a firm believer in the phlogiston theory of combustion.

Antoine Laurent Lavoisier, a French investigator, was the first to show what really happens during ordinary burning. (See Fig. 27.) He used the balance to show that metals gain weight when heated and to prove that the weight gained exactly equals the weight of oxygen added. He showed that matter is not gained or lost during a chemical change, thus giving proof to the theory of the indestructibility of matter. When he heard of Priestley's experiments, he had been studying the rusting of metals in air. He at once came to the conclusion that Priestley's "perfect air" is really a part of ordinary air. To prove his conclusion, he devised the following classical experiment:

In the apparatus of Fig. 28 the retort contained a weighed quantity of mercury and the bell-glass a measured volume of air. The pneumatic trough contained mercury. When Lavoisier heated the mercury in the retort, some of it turned to a red powder, and the volume of the air in the bell-glass was reduced. After 12 days no further action took place even when the heat-

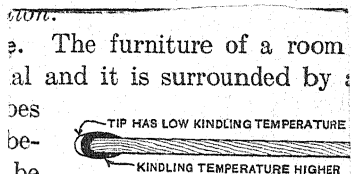
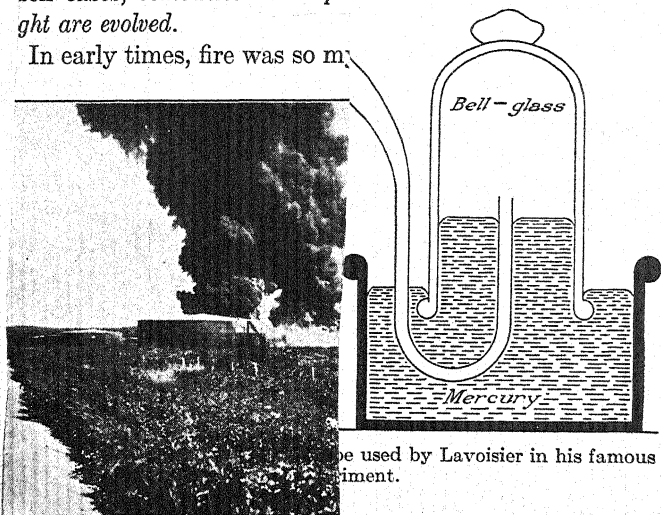


FIG. 29. — Match (longitudinal section).

once takes fire, or begins to burn. This temperature varies with the nature of the substance, and the surface exposed. Phosphorus has so low a kindling temperature that a slight amount of friction raises the temperature enough to kindle it. The match is made of some material with a low kindling temperature. When it is struck, the chemical reaction liberates enough heat to kindle the match-stick. (See Fig. 29.) The burning of the oxygen unites with the carbon of the match-stick to form carbon dioxide.

ing was continued. The mercury in the retort had gained weight, and the volume of the air in the bell-glass had shrunk to four-fifths its former volume. Thus Lavoisier proved that one-fifth of ordinary air is a gas that is capable of uniting with mercury to form a red powder. He named this gas *oxygen*. Good burns, the carbon and shed, Lavoisier then heated the chemically with the oxygen med, more strongly than before, rich cases, *combustion is rapid* *ght are evolved*.

In early times, fire was so m



be used by Lavoisier in his famous experiment.

FIG. 26. — A burning oil tank. The operated which was exactly like part of the cart

Because Lavoisier proved that *ordinary burning is the union of oxygen with some other substance*, he is known as the father of modern chemistry. Despite the plea of one of the friends of Lavoisier, this distinguished scientist was put to death by the guillotine in 1794. The Revolutionists remarked, "France has no need for savants."

Since only about one-fifth of the air is oxygen, substances burn more rapidly in pure oxygen than in air, and some substances that do not burn in air at all, burn vigorously in

oxygen. A *glowing* splinter thrust into a bottle of oxygen bursts into flame. *This serves as a test for oxygen.* Finely divided iron burns in oxygen, giving off dazzling white sparks. Since oxygen is required for ordinary burning, the gas is said to *support combustion*.

**35. Kindling Temperature.** The furniture of a room is made of combustible material and it is surrounded by air containing oxygen, but it does not take fire. Before wood begins to burn, heat must be applied to raise it to a certain temperature. *The lowest temperature at which a substance takes fire, or begins to burn, is called its kindling temperature.* This temperature varies



FIG. 29. — Match (longitudinal section).

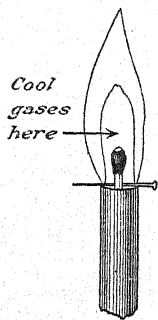


FIG. 30. — Match head in flame shows that combustion occurs at surface only.

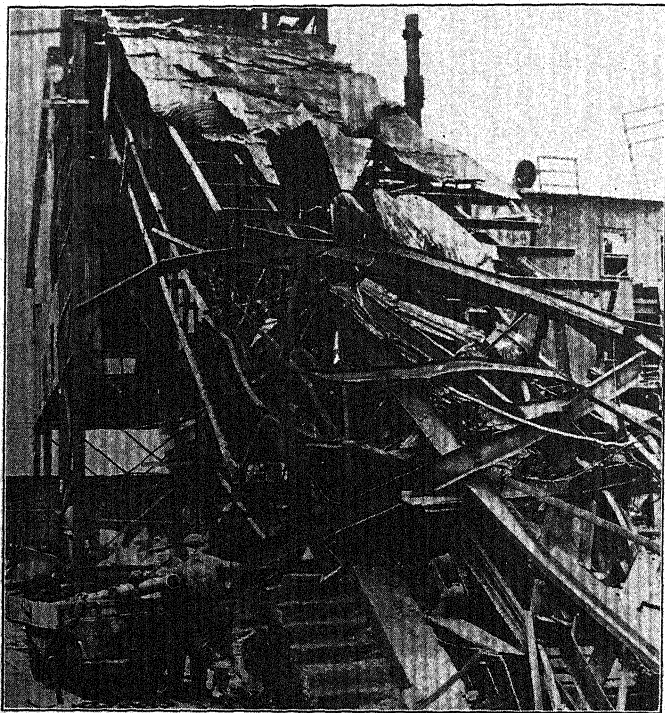
with the nature of the substance, and the amount of surface exposed. Phosphorus, for example, has so low a kindling temperature that a slight amount of friction raises its temperature enough to kindle it. The head of a match is made of some material that has a low kindling temperature. When the head burns, the chemical reaction is *exothermic*, and enough heat is liberated to kindle the match-stick. (See Fig. 29.)

Since in burning the oxygen unites with the substance, combustion can occur at the surface only. A match supported as in Fig. 30 in the center of the flame of a Bunsen burner is not kindled. This shows that such a flame is hollow and that burning occurs only at the surface where the gas comes into contact with the oxygen in the air. This fact may also be shown by momentarily thrusting a sheet of paper down upon the flame. The charred spot on the paper is circular.

It is of interest to study the effect of increasing the surface



of a combustible substance. If we split a block of wood, two new surfaces are exposed to the oxygen and combustion is more rapid. If these pieces are split again still more surface is exposed. Wood shavings and paper burn rapidly because



*Courtesy U.S. Bureau of Mines*

FIG. 31. — This twisted mass of débris bears mute testimony to the violence of dust explosions.

they have such large surface areas. A powdered substance has such an extensive surface that it burns almost instantly, or explosively, if it is loose enough so oxygen can penetrate it readily. Dust scattered through the air of a coal mine, or particles of flour scattered through a flour mill, may explode



if they are ignited or raised to their kindling temperature. (See Fig. 31.) Powdered coal will burn in a manner similar to gas, if the powdered coal is blown by compressed air into the furnace where it is ignited. *One type of explosion may be defined as practically instantaneous combustion throughout the entire mass.*

The carburetor of an automobile mixes gasoline vapor and air in just the right proportion to form an explosive mixture. (See Fig. 32.) As the piston in the cylinder of an automobile moves downward, such a mixture is pushed into the upper part of the cylinder. There the mixture is compressed by the piston as it next moves upward. An electric spark heats the

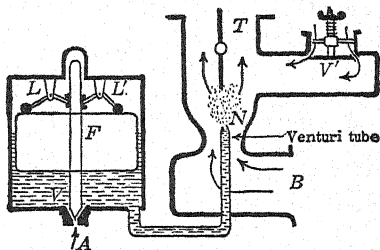


FIG. 32. — Diagram of carburetor.

gaseous mixture to its kindling temperature, the mixture explodes, and pushes the piston downward again with great force. (See Fig. 33.) Thus we utilize the force caused by the *rapid expansion* of exploding gases to drive the automobile. The products formed during an explosion may expand and occupy a space several thousand times their original volume.

**36. Principles Involved in Extinguishing Fires.** We have seen that three things are necessary for combustion: (1) *Combustible material*; (2) *a supply of oxygen*; (3) *the substance must be raised to its kindling temperature*. A fire may be extinguished: (1) *by removing the combustible material*; (2) *by shutting off the supply of oxygen*; (3) *by cooling the substance below its kindling temperature*. The successful application of any one of these principles extinguishes the fire. In large city fires, buildings are often dynamited to make the combustible material inaccessible. Water lowers the temperature of the burning substance and, as the water evaporates,

its vapor shuts off the supply of oxygen. A wet blanket, or a quantity of sand, shuts off the oxygen supply. The effect of lowering the temperature may be seen by holding a copper spiral in a candle flame. The copper conducts the heat away so rapidly that the temperature falls below the kindling point, and the flame is extinguished.

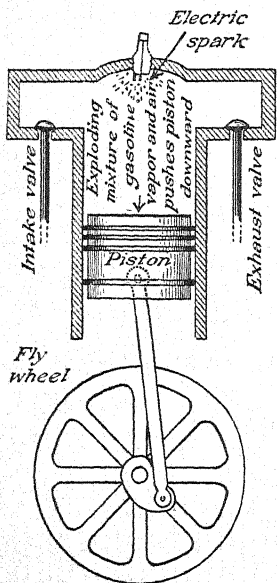


FIG. 33. — Sectional view of a single cylinder gas engine.

**37. How Combustion May Occur Spontaneously.** Several substances oxidize slowly even at the ordinary temperature and some heat is produced. If the air cannot circulate freely to disseminate the heat, or if the substance is a very poor conductor, the accumulation of heat may eventually raise the temperature to the kindling point. Thus the substance takes fire spontaneously. Hay, grain, and coal may oxidize slowly and cause fires by spontaneous combustion. Oily rags thrown in a closet and left undisturbed are a source of danger since the slow oxidation of the oil may heat them to their kindling temperature.

Fires are often started in this way by spontaneous combustion. Metal cans should be provided in machine shops for oily waste. Vegetable and animal oils absorb oxygen slowly and may take fire spontaneously. Linseed oil "dries" by the absorption of oxygen; hence rags used by painters are especially dangerous.

**38. What Products Are Formed by Ordinary Combustion?** If we blow our breath through a clear solution of lime water, a milky precipitate is produced. This reaction, which is

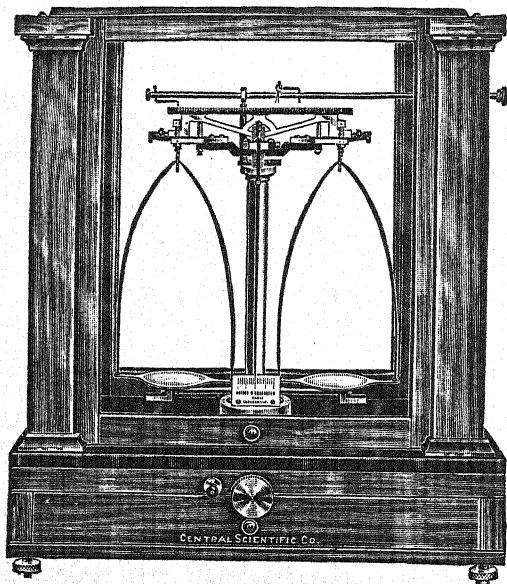
caused by the interaction of lime water,  $\text{Ca}(\text{OH})_2$ , and carbon dioxide,  $\text{CO}_2$ , is a *test for carbon dioxide*. The precipitate formed is calcium carbonate,  $\text{CaCO}_3$ . If we blow our breath against a cold window pane, water condenses on the glass. Both of these products are formed by the "slow fires" that are burning in our bodies at all times. We call it slow oxidation, but oxidation and ordinary combustion differ only in the speed at which they occur. Illuminating gas contains carbon and hydrogen. When burned, it forms water and carbon dioxide. A wax candle, wood, coal, and such fuels as kerosene and gasoline are composed largely of carbon and hydrogen. When these elements in the fuels burn, *both water and carbon dioxide are produced*. The mineral matter present in wood and coal remain as an ash, and small quantities of other products may be formed during combustion.

If there is not sufficient oxygen to burn the carbon in a fuel completely, some carbon monoxide ( $\text{CO}$ ) may be produced. Such incomplete combustion occurs when gasoline burns in an automobile engine, or when fresh fuel is added to our furnace fire and the supply of oxygen is reduced by closing the draft. *Carbon monoxide is a deadly poisonous gas*, whereas carbon dioxide is *not* poisonous.

**39. Weight Changes in Burning.** By the use of the balance Lavoisier learned that mercury increases in weight when it combines with oxygen and forms the red powder, mercuric oxide. (See Fig. 34.) It is easy for students in the laboratory to show that such metals as tin, magnesium, iron, and copper also gain in weight when they are heated in air, or oxidized.

When we burn wood or coal, however, the solid residue (ash) that is left weighs much less than did the original material. This puzzled the believers in the phlogiston theory. If we could collect the gases that go up the chimney when we burn a lump of coal, weigh them, and add their weight to the weight of ash remaining, we would find a decided increase

in weight. In fact, when one ton of pure charcoal is completely burned, it unites with  $2\frac{2}{3}$  tons of oxygen, and forms  $3\frac{2}{3}$  tons of carbon dioxide. In all chemical reactions, the weight of the factors combining exactly equals the weight of the product or products that are formed. *No weight is ever*



*Courtesy of Central Scientific Co.*

FIG. 34. — A small piece of paper may be weighed on a sensitive chemical balance. The balance will show an increase in weight if a line  $\frac{1}{4}$  in. long is drawn on the paper with a lead pencil.

*gained or lost in a chemical reaction*, a fact that is known as the LAW OF THE CONSERVATION OF MATTER.

**40. What Is The Nature of Incombustible Material?** Some materials do not burn at all, and others are quite *flammable* or combustible.<sup>1</sup> See note below. It is easy to

<sup>1</sup> NOTE. Strange as it may seem, the words *flammable* and *inflammable* have the same meaning. A person learning the English

understand why water, for example, does not burn. The hydrogen in the water already holds all the oxygen it can. As a rule, oxides are incombustible. Water and carbon dioxide make excellent fire extinguishers. The oxides of calcium, magnesium, and of silicon (sand, or  $\text{SiO}_2$ ) make good material for lining furnaces or for fire-proofing.

**41. How Oxygen Is Related to Life.** Oxygen is one of the most important elements. It may justly be called the life-giving element. Without oxygen animals could live only a few minutes. Taken in through the lungs, it is carried by the hemoglobin of the blood to all parts of the body. It oxidizes a part of our food, thus supplying us with warmth and furnishing us with heat energy. Fishes take oxygen from the air that is dissolved in water. Even plants need oxygen for ordinary respiration. In

animal bodies, oxygen slowly oxidizes the waste tissues so they may be readily removed by the organs of excretion. Carbon dioxide and water vapor, waste products of oxidation, are exhaled from the lungs.

language would suspect that the latter meant non-combustible. Since accidents have occurred in our industrial plants on account of this error, the Bureau of Standards is trying to have the word *flammable* used in marking all combustible materials.



*Courtesy of Mine Safety Appliances Co.*

FIG. 35. — The wearer carries his own supply of oxygen.

**42. One Form of Decay Is An Oxidation Process.** In the presence of bacteria, plant and animal tissues slowly oxidize during the processes of decay. Several reactions occur, but some water and carbon dioxide are produced. Dry wood



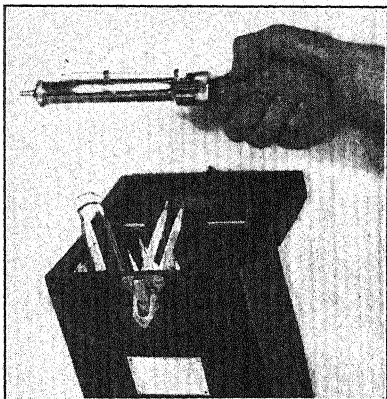
*Courtesy U.S. Bureau of Mines*

FIG. 36. — Men equipped with oxygen apparatus used in mines or for rescue work. Note white mice in cage carried by the man at the right.

and dried foodstuffs do not decay, because bacteria need moisture for their growth.

**43. Oxygen Has Many Uses.** 1. *In Special Occupations.* Very often it becomes necessary for a fireman to enter a building filled with smoke, or for a miner to enter a mine filled with poisonous or suffocating gases. Under such circumstances they make use of an oxygen helmet. (See Fig. 35.) Oxygen under pressure is carried in cylinders at

the back, whence it is supplied through a reducing valve to the breathing bag which is carried on the wearer's chest. Or the oxygen may be generated by chemicals and supplied through a flexible tube to a mask that fits over the nose and mouth of the wearer. Figure 36 shows a group of men equipped with oxygen apparatus testing for poisonous gases in a coal mine. The one at the right has a cage of white mice. These animals and canaries are often used in this way since they are very susceptible to poisonous gases. A chemical detector is now used extensively for this purpose. (See Fig. 37.) Divers sometimes are equipped with self-contained oxygen apparatus. The War Department has found that aviators ascending to high altitudes become faint or weakened because the air is too rare



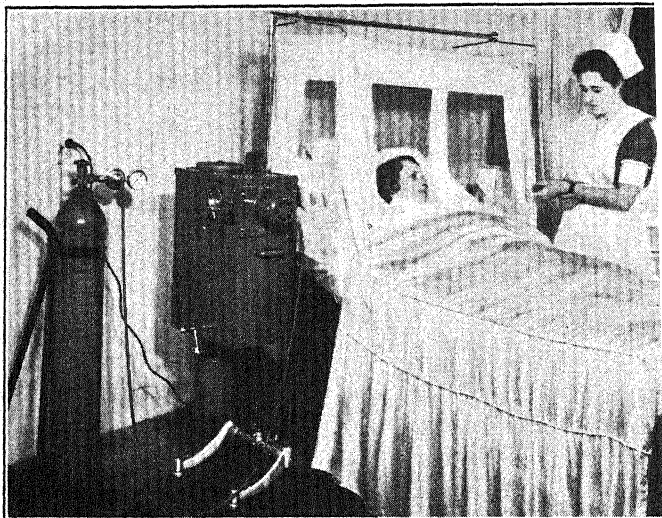
*Courtesy U.S. Bureau of Mines*

FIG. 37.—The tube contains iodine pentoxide (Hoolamite) which shows a color change varying in depth with the amount of carbon monoxide present in air.

to supply enough oxygen. Therefore rules are enforced requiring all aviators flying at a height of more than 10,000 feet to carry a supply of oxygen. It is also of interest to note that a gas engine loses about 60% of its efficiency at an elevation of 20,000 feet, because the supply of oxygen is reduced unless a supercharger is used.

2. *For Resuscitation Work.* Pure oxygen is often given to persons suffering from pneumonia and in other cases when the person is too weak to inhale the necessary volume of air. In cases of asphyxiation from inhaling smoke or other suffo-





*Courtesy of McKesson Appliance Co.*

FIG. 38. — Oxygen from the cylinder at the left is supplied to the patient under the tent.

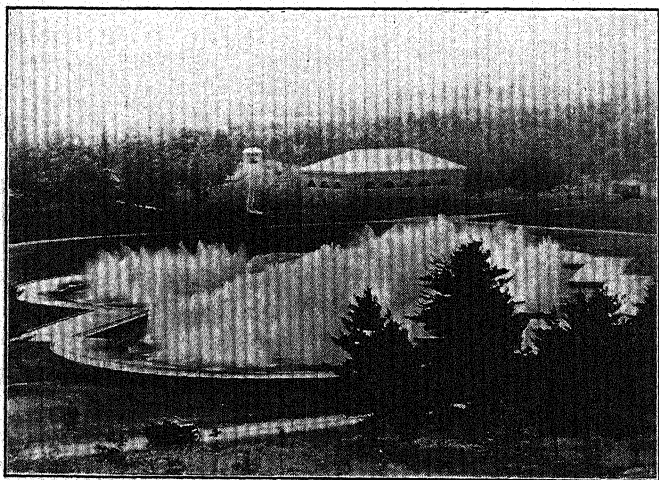


FIG. 39. — Aëration reservoir for purifying water.



cating gases, or from electric shock, an oxygen tent is used. An electric motor keeps the tent supplied with air, and oxygen is added in the desired proportion (see Fig. 38). As many as 100 cu. ft. of air per minute may be supplied to the patient. A flow-meter is used to regulate the amount of oxygen being supplied. It may supply 14 liters per minute.

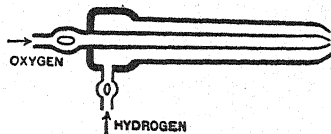


FIG. 40. — Oxy-hydrogen blowpipe.



FIG. 41. — Robert Hare (1781-1858) was an American chemist, writer, and inventor. He made the first electric furnace, in which he prepared graphite and calcium carbide.

### 3. For Purification.

Fresh air and sunlight are the best disinfectants. Oxygen in the air is believed to be a very valuable aid in destroying bacteria. Rivers containing sewage are purified in flowing considerable distances by contact with the oxygen in the air. In the sewage disposal plants of some cities the sewage is sprayed into the air to be purified by the oxygen. Fountains, cascades, and other devices are used to aid in purifying city water supplies.

Figure 39 shows the aëration reservoir at Ashokan

where some of the water used to supply New York City is aërated. The water flows 85 miles through an aqueduct 7 feet in diameter.

4. *For Blowpipe Work.* In 1801 Robert Hare, an American chemist, invented the oxy-hydrogen blowpipe. (See Fig. 40.) This blowpipe consists of two concentric tubes. Hydrogen from a storage cylinder passes through the outer

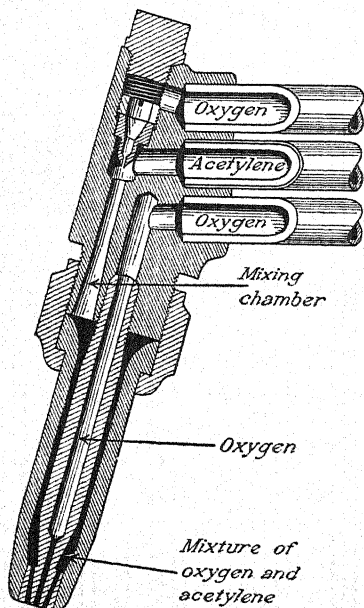


FIG. 42. — Oxy-acetylene blowpipe.

tube and is lighted at the tip of the blowpipe. The oxygen, passing through the inner tube, combines with the hydrogen and produces a very hot flame. Hare succeeded in melting platinum, sand, aluminum oxide, and other refractory substances. He modestly remarks, "Had I sufficient confidence in my own judgment, I should declare that gold, silver, and platinum were thrown into a state of ebullition by exposure on carbon to the gaseous flame." (See Fig. 41.) The temperature of the oxy-hydrogen flame is estimated to be about  $2300^{\circ}\text{C}$ . It still finds use in melting platinum and quartz and in the fusion of aluminum oxide for making artificial rubies. Drummond produced the *lime light* by directing the flame from such a blowpipe against a stick of lime. The lime does not melt, but it is heated white hot. Any substance thus heated until it *glows* is said to be *incandescent*. Before the advent of the electric arc, the lime light was much used for stage illumination and for stereopticon work.

The oxy-acetylene blowpipe, Fig. 42, has largely taken the place of the oxy-hydrogen blowpipe. It gives a much hotter

flame, estimated at from 3400 to 3700° C. This blowpipe is extensively used for cutting metals. (See Fig. 43.) A similar blowpipe is used for welding metals.

#### OZONE

44. Preparation of Ozone. In the ozonizer shown in Fig. 44 the tubes are covered with layers of tin foil. The

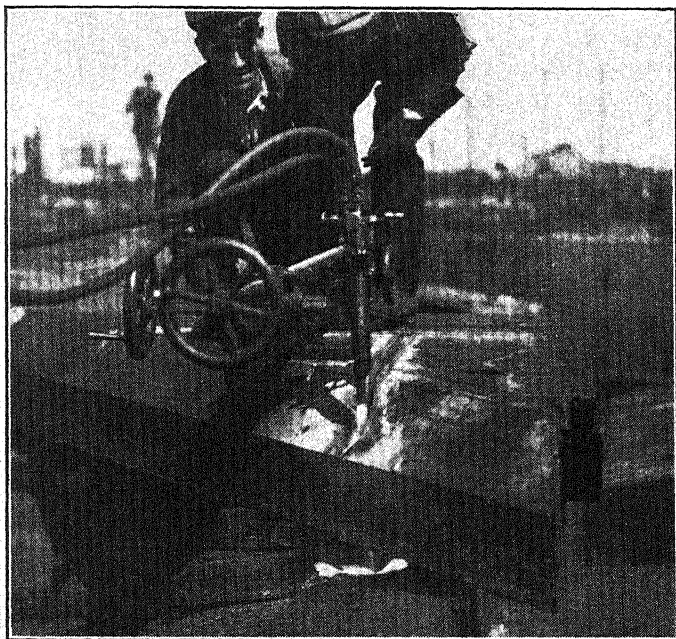


FIG. 43. — Cutting through 12-in. armor plate with the oxy-acetylene flame.

inner layer of foil is then connected to one terminal of an induction coil, or a coil for producing electric sparks, and the other layer is connected to the other terminal. Thus there will be a brush discharge, or a leakage of electricity across the tubes from one layer of tin foil to the other. When oxygen

is passed through the tube, a part of the oxygen is converted into *ozone*. Some ozone is formed in the air by the lightning flash during an electrical storm. It is also produced by the slow oxidation of the sap of pine trees in pine forests, or during the slow oxidation of phosphorus.

**45. What Is the Nature of Ozone?** It is not unusual in chemistry for the same element to exist in two or more different forms. Such an element seems to have a dual personality, or to live a kind of Dr. Jekyll and Mr. Hyde existence. Each form is called an *allotropic* modification of the other. This word comes from the Greek (*allos*, "other";

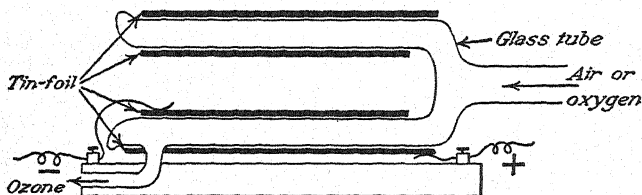
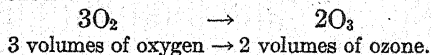


FIG. 44. — Ozonizer.

*tropos*, "turn" or "direction"). Hence it is possible to turn one form into the other. To change oxygen to ozone, we add electrical energy to it. Three volumes of oxygen form two volumes of ozone.



**46. Properties and Uses of Ozone.** Unlike oxygen, ozone has an irritating odor. It can be smelled in a room where an electrical machine has been running for some time. Ozone is heavier than oxygen, and considerably more soluble in water. It is one of the most vigorous oxidizing agents known. It destroys bacteria and causes many colors to fade rapidly. It attacks silver and mercury, forming black oxides of these metals. At a high temperature, it is converted into oxygen.

Ozone has been used to some extent for bleaching wood

pulp, textile fibers, oils, and waxes. In Lille, Paris, Lenin-grad, and several other European cities, ozone is used to purify the water in city reservoirs. Some ozonized water is sold in certain cities of the United States under the name "Electrified water." Ozone has one decided advantage over other bleaching and disinfecting agents. As it bleaches or destroys bacteria, only oxygen is left. Attempts have been made to use ozone in ventilating systems for large buildings. But here it is irritating to human beings, if it is used in large enough quantities to destroy bacteria. It is useful, however, in destroying the odors that arise in slaughter-houses, cold-storage rooms, restaurants, and kitchens.

## SUMMARY

Oxygen is the most abundant element. It is found in air, in water, and in many rocks of the earth's crust.

Priestley first prepared oxygen by heating *mercuric oxide*. In the laboratory it is prepared by heating a mixture of *potassium chlorate* and *manganese dioxide*. Commercially it is obtained from water by *electrolysis* or from *liquid air*.

Oxygen is a colorless, odorless, tasteless gas. It is slightly soluble in water, and slightly heavier than air. Oxygen is one of the most active elements, especially at high temperatures.

A *catalytic agent* is a substance that aids chemical action without being permanently changed itself.

The process by which oxygen unites with some other substance is called *oxidation*. The compound that supplies the oxygen is called an *oxidizing agent*. The substance upon which the oxygen acts is said to be *oxidized*. The product formed as a result of oxidation is called an *oxide*.

*Ordinary combustion is rapid oxidation*. Light and noticeable heat are evolved. Before burning can occur, the combustible material must be heated to its kindling temperature. Lavoisier, a French chemist, was the first to explain the true nature of combustion. He is commonly called the "Father of Chemistry."

Three things are needed for combustion: (1) *combustible*

material; (2) a supply of oxygen; (3) the material must be heated to its kindling temperature. Fires are extinguished by eliminating any one of the three essential factors.

The products of ordinary combustion are *water* and *carbon dioxide*. Substances increase in weight when burned, because the oxygen with which they unite has weight.

Oxygen is essential to plant and animal life. It plays a part in decay. It is used in the oxy-hydrogen and the oxy-acetylene blowpipes; it finds use in hospitals; it is carried by miners engaged in rescue work, and by aviators.

Ozone is a very active form of oxygen. It is a good bleaching and purifying agent.

## QUESTIONS

### GROUP A

1. Why would fishes die if put in an aquarium of water which had been boiled and subsequently cooled?
2. In preparing any element, what things would need to be considered in the choice of the raw materials?
3. Why are catalysts of so much value to manufacturers?
4. What products are formed by burning each of the following: tin, copper, phosphorus, magnesium, sulfur, carbon, and iron?
5. How would you test a bottle of gas to distinguish oxygen from air? To distinguish between oxygen and carbon dioxide?
6. Paper, wood, and coal are usually added successively when starting a hard coal fire. Explain.
7. Why does a book or a magazine burn so slowly when closed and so rapidly when opened?
8. Why is a candle flame extinguished by blowing? Why does blowing a fire make it burn more vigorously?
9. Why is a spark in a flour mill likely to cause an explosion?
10. Which should you use to put out a gasoline fire, water or sand? Explain.
11. When baking soda is heated, it gives off carbon dioxide. Do you think baking soda would make a good fire extinguisher? Explain.
12. Pyrene fire extinguishers contain carbon tetrachloride, a volatile liquid that does not burn. Explain how it puts out a fire.

13. Carbon tetrachloride is quite as good for dry cleaning and removing stains as gasoline. What advantage has it over gasoline for that purpose?

14. Can you think of any metals that would not gain in weight when heated in air? If so, name them.

15. Why is no ash formed when fuel gas burns?

16. Automobile shops frequently use oxygen. For what purposes?

17. Explain why water and carbon dioxide do not burn.

18. What would be the best thing to do if your clothing caught fire?

19. When a paint hardens, the linseed oil takes oxygen from the air and forms a tough, resinous skin. What kind of a chemical would you add to a paint to make it "dry" faster?

20. Why should wood and such metals as iron be kept well-painted?

21. Why should oily wastes be kept in metal containers in shops and factories?

22. What property of oxygen makes it possible to collect the gas by water displacement? Should bottles of oxygen gas be kept mouth upward or mouth downward? Explain.

#### GROUP B

23. What changes would occur in nature if the air were pure oxygen? Do you think it would be of advantage to administer oxygen to a football team just before a game?

24. From the formulas note the difference between potassium chloride and potassium chlorate. How would you expect a nitride to differ from a nitrate? Or a sulfide from a sulfate?

25. When one end of a splinter is thrust into a flame, why does not the splinter burn along its entire length as soon as one end is kindled?

26. Since powdering a substance makes it burn more rapidly, why is it so difficult to burn coal dust in a furnace?

27. If our atmosphere were composed of illuminating gas, do you think oxygen would burn in it? Are the terms "combustible" and "supporter of combustion" interchangeable?

28. Why is a gas engine called an internal combustion engine?



29. What is meant by saying that the cylinders of a gas engine are flooded?

30. Sir Walter Raleigh is said to have made a wager with Queen Elizabeth that he could tell the weight of smoke. He weighed a pipe filled with tobacco, smoked it, and then weighed it again. He gave the difference as the weight of the smoke. Had Queen Elizabeth known chemistry, how could she have proved that he was wrong?

31. Cork for making linoleum is ground between stones to a very fine dust. If the cork is not supplied continuously to the revolving stones, an explosion may occur. Explain.

## PROBLEMS

### GROUP A

1. If water is 88.88% oxygen, how many liters of oxygen can be prepared from 100 gm. of water by electrolysis?

2. How many grams of oxygen can be obtained from 5 gm. of potassium chlorate, which is 39% oxygen? How many liters would the oxygen occupy at standard temperature and pressure?

### GROUP B

3. Suppose you burn 10 tons of coal during the winter. If that coal is 80% carbon, how many tons of carbon dioxide gas will go up your chimney? Hint: See Section 39.

4. Suppose the coal in Problem 3 contains 4% of hydrogen. How many gallons of water would be formed by its complete combustion? (A gallon of water weighs about 8 lb.) Hint: The hydrogen in water is only 11.11% of the total weight.

## SUPPLEMENTARY PROJECTS

Prepare a report on the life and work of Joseph Priestley or of Antoine Lavoisier.

Be prepared to give an historical and explanatory account of the phlogiston theory of combustion.

References: Any good encyclopedia.

MOORE, F. J., *History of Chemistry*. McGraw-Hill.



**Concentrated lye, or caustic soda.**  
properties are quite the opposite

## HY

It is similar to sodium, but it is placed on water, it liberates heat the heat of the reaction is hydrogen, which burns as fast as it is a compound. Some other metals attack water, however, interacts more slowly.

**Occlusion.** The absorption of hydrogen, which burns as fast as it is a compound.

**Diffusion.** The intermingling motion.

**Reduction.** De-oxidation, Some other metals attack water, however, interacts more slowly.

**Hydrogenation.** The addition of hydrogen, which burns as fast as it is a compound.

**Incandescence.** Heated to glowing; generally to a white heat.

**Swage.** To shape metals by the hydrogen from water. One is designed for the purpose.

**47. Where Hydrogen Is Prepared.** When heat, a reaction represented by the following takes place:

wealthy recluse whose sole work is to show that water is not a compound, but a mixture of hydrogen and oxygen. His most successful work showing that water is a compound is set free when acids interact with it.

This gas was not called hydrogen until 1781, when it was named by Lavoisier. Conditions may be used, and any one of them may be used, and any one of them may be used.

an abundant element, but it is widely distributed. One-ninth of water by weight is hydrogen, and all acids contain hydrogen. Hydrogen is present in all plant and animal tissues. Nearly all our fuels — gas, wood, and coal — contain hydrogen.

**48. How Hydrogen Is Prepared.** Since hydrogen is widely distributed, several methods of preparing it are known. In

nearly all cases, however, the hydrogen is obtained either from *water* or from some *acid*.

1. *From water.* (By electrolysis.) This method is quite extensively used for preparing hydrogen in the United States

and in Germany. The process was discussed in Section 29. If we consider hydrogen as the main product, then oxygen becomes the by-product.

it again. He gave the difference. Had Queen Elizabeth known she proved that he was wrong?

31. Cork for making linoleum is very fine dust. If the cork is not revolving stones, an explosion may

#### PROBLEM

##### GROUP

1. If water is 88.88% oxygen can be prepared from 100 gm. of w

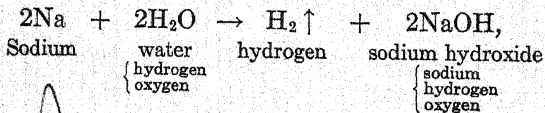
2. How many grams of oxygen of potassium chlorate, which is 39 would the oxygen occupy at stand

##### GROUP

3. Suppose you burn 10 tons that coal is 80% carbon, how many will go up your chimney? Hint: 8

4. Suppose the coal in Problem How many gallons of water would combustion? (A gallon of water weighs hydrogen in water is only 11.11%

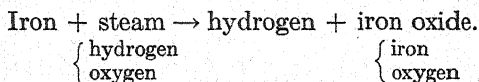
2. *From water.* (By substitution.) Metallic sodium is a white metal, soft enough to be cut easily with a knife, and light enough to float on water. But it has one chemical property that is even more interesting. It is so active chemically that, when placed on water, it interacts vigorously with the water, skimming around on the surface, and liberating hydrogen gas with a hissing sound. This continues until each sodium atom has substituted itself for one of the atoms of hydrogen present in a molecule of water. The following equation,



shows clearly that an atom of sodium displaces one of the hydrogen atoms from a molecule of water, and unites with the remaining hydrogen and oxygen atoms to form *sodium hydroxide*. If we evaporate the *excess* water, a white caustic solid is left. This solid, sodium hydroxide, is familiar to most persons under the name *concentrated lye*, or *caustic soda*. Chemists call it a *base*. Its properties are quite the opposite to those of an *acid*.

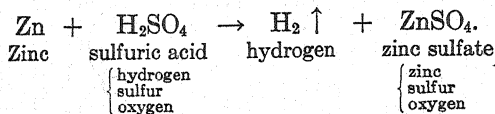
Potassium is a metal that is similar to sodium, but it is even more active. When it is placed on water, it liberates hydrogen with such vigor that the heat of the reaction is sufficient to kindle the hydrogen, which burns as fast as it is set free from the water. Some other metals attack water in a similar manner. Calcium, however, interacts more slowly than sodium.

Magnesium decomposes boiling water slowly. At a high temperature, iron will liberate hydrogen from water. One commercial process for making hydrogen consists in passing steam through a tube containing finely divided iron. When the iron is heated to a red heat, a reaction represented by the following word equation takes place:



3. *From acids, by substitution.* (Usual laboratory method.) All acids contain hydrogen, which may be set free by certain metals. Several different acids may be used, and any one of quite a number of metals. Sulfuric acid is a heavy, oily liquid. If we add one part of this *concentrated* acid to five or six parts of water, the *dilute* acid thus formed will attack zinc or iron vigorously. The speed at which the hydrogen is evolved depends upon the amount of surface the metal exposes, the temperature, the strength of the acid solution, the kind of metal used, and its purity. Pure zinc interacts

very slowly. In ordinary commercial zinc there is generally enough carbon present to accelerate the action. Figure 46 shows one type of apparatus commonly used in the laboratory for the preparation of hydrogen. Zinc is put in the bottle and either sulfuric or hydrochloric acid is added through the thistle tube. The hydrogen is collected by water displacement. The action is as follows:



It is customary to say that the metal *dissolves* in the acid, but the statement is incorrect. In reality, the metal inter-

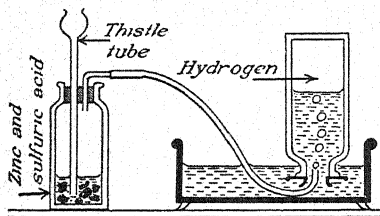


FIG. 46. — Laboratory apparatus for preparing hydrogen.

acts with the acid, liberating hydrogen as a gas, and forming a salt, zinc sulfate, which dissolves in the excess water. The metal loses its properties, but it also destroys the acid. One often hears a plumber when making a soldering fluid speak of

adding zinc to an acid to "kill" the acid. If we evaporate the excess water that is left after the action in the hydrogen generator has stopped, we shall have a white, crystalline solid called *zinc sulfate*. The equation shows us that the zinc has merely substituted itself for the hydrogen of the acid.

**49. Physical Properties.** Hydrogen is a colorless, odorless, tasteless gas. It is the lightest gas known, being only one-fourteenth as heavy as air. One liter at standard conditions weighs almost 0.09 gm. Hydrogen is less soluble in water than oxygen.

In 1898 Dewar succeeded in liquefying hydrogen by reducing the gas to a very low temperature and subjecting

it to a high pressure. Liquid hydrogen is clear and colorless, only one-fourteenth as heavy as water. Its boiling point is  $-252.5^{\circ}\text{C}$ . When a part of the liquid is evaporated rapidly, the remainder freezes to an ice-like solid.

Liquids and gases have the property of intermingling through the pores of membranes. (See Fig. 47.) This is called *osmosis*. Hydrogen diffuses in this manner more rapidly than any other gas, because the molecules of a light gas move at a high velocity. This makes it difficult to keep hydrogen in containers. Rubber balloons filled with hydrogen soon collapse due to the rapid escape of the hydrogen through the pores of the rubber.

Dr. Harold C. Urey was awarded the Nobel prize in 1934 for his research work with 'heavy water' and 'heavy hydrogen,' which is called *deuterium*. In its chemical behavior deuterium is much like ordinary hydrogen, but it is twice as heavy. It combines with oxygen to form 'heavy water.'

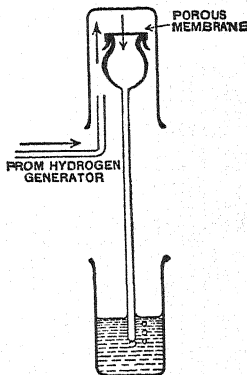
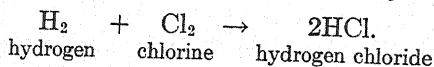


FIG. 47. — Hydrogen readily passes through membranes by osmosis.

**50. Chemical Behavior of Hydrogen.** *Hydrogen* burns with a very hot, pale blue, nearly invisible flame, forming water as its *only* product of combustion. (See Fig. 48.) We may show that *hydrogen does not support combustion* by thrusting a blazing splinter up into a bottle of hydrogen, held mouth downward, as shown in Fig. 49. The hydrogen is ignited and burns at the mouth of the bottle, but the burning splint is extinguished.

Hydrogen is not a very active element. No action occurs when we mix hydrogen and oxygen at room temperature. If the mixture is heated to a temperature of  $800^{\circ}\text{C}$ ., or if a lighted match is brought into contact with it, the gases

unite with explosive violence. Hydrogen and chlorine do not combine when they are mixed in the dark, but they unite explosively in direct sunlight, forming *hydrogen chloride*.



Under suitable conditions hydrogen combines with nitrogen and forms ammonia, a very important compound. The fol-

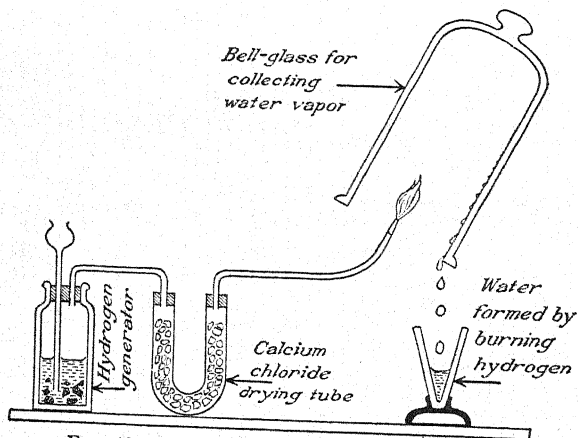
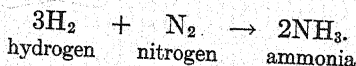


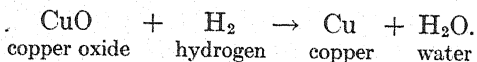
FIG. 48. — As hydrogen burns, water is formed.

lowing equation shows that the chemical action is merely the direct union of the two elements:



The commercial process for making ammonia, which was developed by a German chemist by the name of Haber, will be discussed in a later chapter. It is difficult to make hydrogen combine with metals, but it has been accomplished in certain cases. Some *hydrides* have been formed. An alloy of lead and sodium is sold under the name of *hydrone*. It liberates hydrogen when added to water, and finds use in preparing hydrogen in small quantities.

**51. What Is Meant by Reduction?** If we heat a piece of sheet copper in air, a black scale of copper oxide forms on the surface. If we put this copper oxide in a glass tube, as shown in Fig. 50, and pass *dry* hydrogen over it while the copper oxide is being heated, the hydrogen will remove the oxygen from the copper oxide, unite with it, and form water. The U-tube contains calcium chloride, which dries the hydrogen by absorbing any water that may have been carried over from the generator. Such *abstraction of oxygen from a compound is called reduction*. The hydrogen serves as a *reducing agent*. The equation follows:



From these illustrations we see that oxidation and reduction are opposite processes. Furthermore, it is impossible to

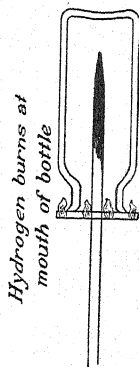


FIG. 49. — Hydrogen burns, but it does not support combustion.

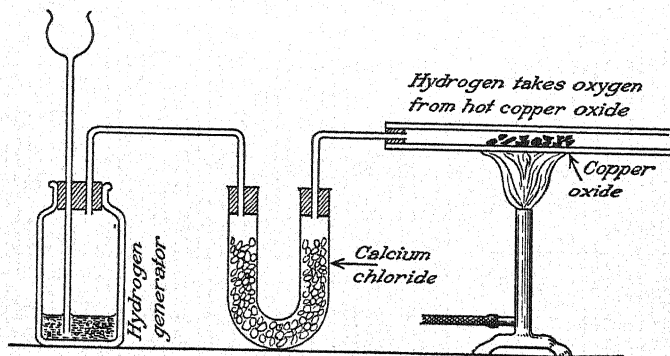


FIG. 50. — The hot hydrogen reduces the copper oxide to metallic copper.

have one take place without the other. In the reaction represented by the equation, the copper oxide was the



oxidizing agent and the hydrogen was oxidized; the hydrogen was the reducing agent, and the copper oxide was reduced to metallic copper.

**52. How One May Test for Hydrogen.** The most conclusive test for hydrogen depends on the fact that hydrogen burns with a nearly colorless flame and *forms nothing but water* as a product of its combustion.

**53. Replacement of Metals.** *Some metals replace others from their compounds.* In our study of the preparation of hydrogen, we learned that several metals will replace hydrogen from water or from acids. Potassium, however, was more vigorous than sodium; sodium liberates hydrogen from water faster than calcium does; and calcium faster than magnesium. It is possible to arrange the metals in the *order of their activity*. In the accompanying replacement series table, we find hydrogen grouped with the metals. Experiment shows that all the metals that stand above hydrogen in the table will replace hydrogen from acids, such as hydrochloric and sulfuric. The metals that stand below hydrogen in this table are not affected by dilute acids. In Section 27 it was shown that zinc would replace either

**REPLACEMENT  
SERIES**

Potassium  
Sodium  
Calcium  
Magnesium  
Aluminum  
Zinc  
Iron  
Nickel  
Tin  
Lead

**HYDROGEN**

Copper  
Mercury  
Silver  
Platinum  
Gold

lead or tin. Any metal that stands above another in this replacement series will replace that metal from its compounds. For example, potassium will replace any other metal in the group. Sodium replaces all but potassium. Zinc replaces any metal that stands below it, but it does not replace any metal that stands above it. The student will find the replacement series table helpful throughout his chemistry course.

**54. How the Hydrogen Molecule Is Split into Atoms.** We have learned that the molecule of a gaseous element contains two atoms. Dr. Irving Langmuir learned how to split up hydrogen molecules and produce *atomic hydrogen*. The hydrogen gas is passed through an electric arc in which the electrodes are made of tungsten, the metal that is used for the filaments of our electric lights. (See Fig. 51.) The heat of the electric arc splits the hydrogen molecules into atoms. Tremendous energy is used to accomplish this dissociation.

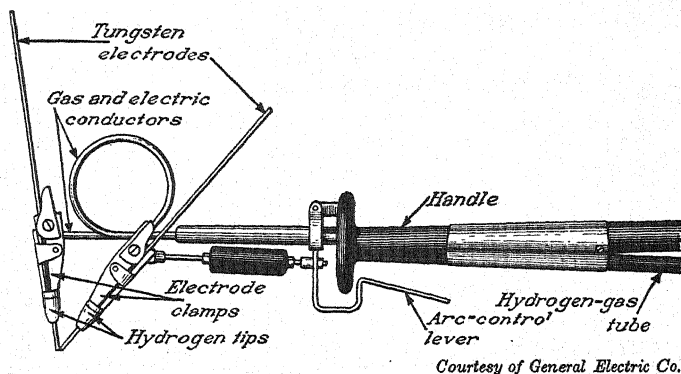
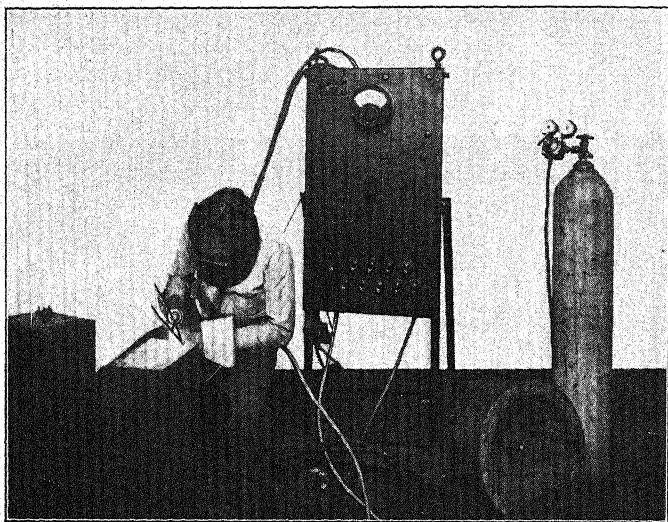


FIG. 51. — The tungsten arc apparatus for using atomic hydrogen.

As the atoms leave the electrode, they reunite to form hydrogen molecules, which later combine with the oxygen around the arc. All the heat that was absorbed from the arc in breaking up the molecule is liberated when the atoms recombine. This heat, added to that produced by the burning of the hydrogen molecules, gives the hottest flame or arc that man has been able to produce. The temperature is estimated at  $4000^{\circ}\text{C}$ . The *atomic-hydrogen arc* is used for cutting and welding metals. (See Fig. 52.)

**55. Hydrogen Has Many Uses.** There are several ways in which hydrogen is utilized. A study of its applications

affords us excellent examples of the manner in which the uses of a substance depend upon its *special* properties.



*Courtesy of General Electric Co.*

FIG. 52. — Use of the atomic-hydrogen arc for welding.

1. *For its buoyancy.* Since hydrogen is the lightest gas known, we would expect it to find use in filling balloons and

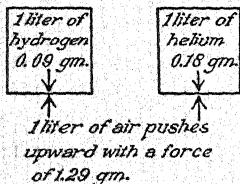


FIG. 53. — The upward push of the air is the same in both cases, but the helium weighs more.

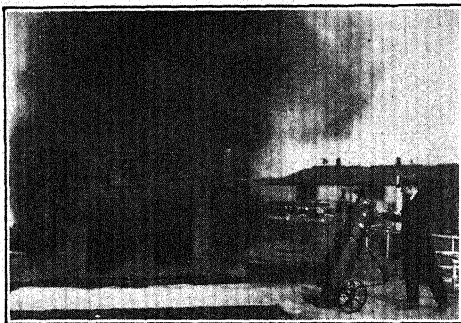
dirigibles. Its so-called lifting power per liter is equal to the difference between the weight of 1 liter of air (1.29 gm.) and 1 liter of hydrogen (0.09 gm.). (See Fig. 53.) That means that the buoyant force on a toy balloon of one liter capacity, when filled with hydrogen, is 1.2 gm. There are 1000 liters in 1 cubic meter.

Hence for every cubic meter capacity a balloon filled with hydrogen has a lifting power of 1.2 kilograms, or 2.64 lb. Military dirigibles of the Zeppelin



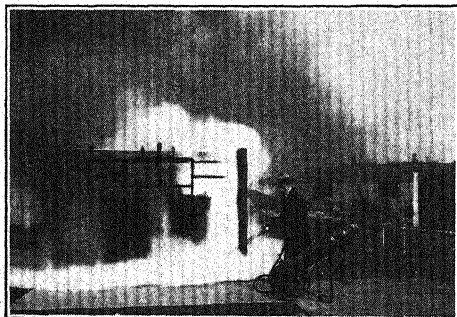
Courtesy of Major H. Lee Wells, Jr., 3507 Jones St., Omaha, Neb. Copyright, 1935

The *Explorer II* almost ready for its flight into the stratosphere. In the small gondola suspended from the huge balloon, Captains Stevens and Anderson ascended to the record height of 72,395 feet on Nov. 11, 1935. (See *National Geographic Magazine*, Jan. 1936.)



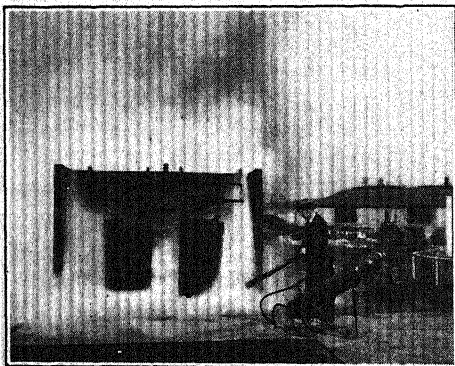
*Courtesy of Pyrene Mfg. Co.*

This picture shows a cylinder of liquid carbon dioxide being used to extinguish a transformer fire. The dikes around the base of the transformer are filled to a depth of one inch with a mixture of gasoline and fuel oil. Thirty seconds after the fire started.



*Courtesy of Pyrene Mfg. Co.*

The 50-lb.-capacity cylinder is wheeled to the fire and the valve is opened to release the pressure. One cu. ft. of liquid carbon dioxide then expands and forms about 450 cu. ft. of gas, which surrounds the fire and smothers it by blanketing. Five seconds after the gas is applied.



*Courtesy of Pyrene Mfg. Co.*

The gas is non-conducting and the electricity from the transformer is not dangerous to the operator. The rapid expansion of the gas cools some of it so much that clouds of carbon dioxide snow are formed. In ten seconds the fire is snuffed out completely.



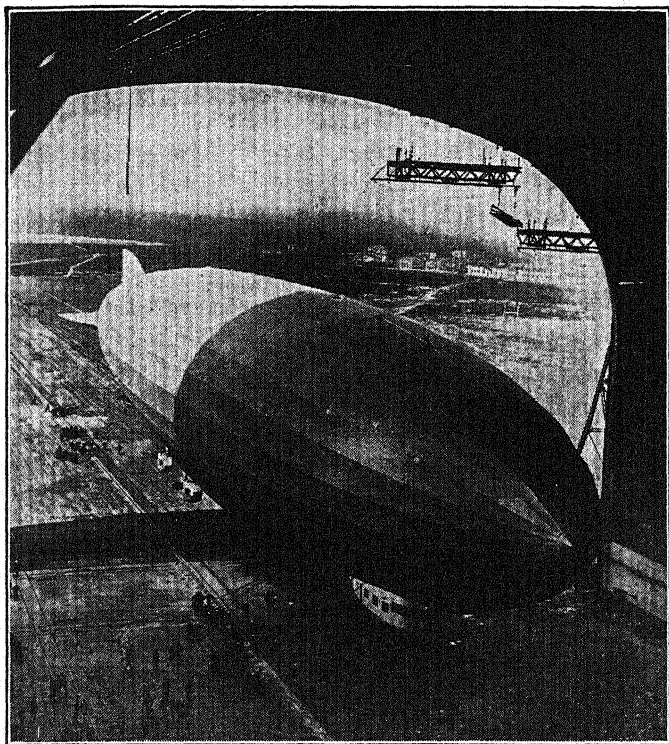


FIG. 54. — The *Los Angeles* entering the hangar at Lakehurst. This dirigible is 656 ft. long, 90 ft. in diameter, and almost 102 ft. high. The gas bags hold 2,472,000 cu. ft. of gas. The *Los Angeles* weighs 91,000 lb. and can carry a load of 88,190 lb.

type have gas bags that hold several thousand cubic meters. Some of the Navy blimps are now filled with helium, a gas that is non-flammable. Helium is not quite 93% as efficient as hydrogen.

2. *As a reducing agent.* In Section 51 we learned that hydrogen can take oxygen from copper oxide. Hydrogen is capable of reducing the oxides of the less active metals, such as copper, tin, lead, zinc, and iron. Reduction is one of the

most important processes in chemistry, because many metals are found in nature as oxides. In the extraction of such metals from their ores, a reducing agent is used to take the oxygen from the oxides. Carbon, however, is cheaper and more convenient to use than hydrogen. It is generally used in the form of coke.

In some cases a metal needs to be worked in an atmosphere free from oxygen. The tungsten used for making filaments for electric bulbs is swaged and prepared for drawing by heating in a hydrogen furnace to prevent oxidation.

3. *As a fuel and illuminant.* Nearly all our fuels contain hydrogen, either free or combined. Coal gas and oil gas contain hydrogen in quantity. The water gas, which is now manufactured so extensively, contains nearly 40% hydrogen. In the chapter on oxygen we learned that hydrogen is used with oxygen as a fuel in the oxy-hydrogen blowpipe. If hydrogen is used alone, it is not satisfactory for illuminating purposes, because its flame is nearly colorless. It is satisfactory as an illuminant only in those cases where its heat may be used to heat some object, such as a piece of lime or a Welsbach mantle, to incandescence.

4. *For making hydrogen compounds.* Increasing quantities of hydrogen are being used in the manufacture of ammonia by the Haber process. Wood alcohol, or *methanol*, is now extensively manufactured by combining hydrogen and carbon monoxide in the presence of a suitable catalyst.

5. *For hardening oils.* Many American housewives prefer solid fats to oils for cooking purposes. Analysis shows that there is no difference between the composition of a solid fat, such as suet, and an oil, such as cottonseed oil, except that the former contains more hydrogen atoms per molecule than the latter. Sabatier, a French chemist, discovered that hydrogen will combine with an oil to make a solid fat, provided finely divided nickel is used as a catalyst. The process is called *hydrogenation*. Millions of pounds of cottonseed oil are



*hydrogenated*, or hardened, every year in the United States in the manufacture of lard substitutes. "Crisco" and "Snowdrift" are examples of cooking fats made by this process. Peanut oil and cocoanut oil are also hardened by this process for use in making the various "nut margarines," or butter substitutes. Some fish oils lose their odor when hydrogenated and become suitable for use in making soap. In the refining of petroleum, hydrogen is used to increase the yield of gasoline.

## SUMMARY

Hydrogen is found in water and in all acids. It is found also in all plant and animal tissues.

Hydrogen is prepared commercially by the *electrolysis of water* and by *passing steam over red-hot iron*. In the laboratory, it is prepared by *substituting a metal for the hydrogen in water*, or for the *hydrogen in an acid*.

Hydrogen is an odorless, colorless, tasteless gas. It is only slightly soluble in water. It is the lightest gas known, being only one-sixteenth as heavy as oxygen.

Hydrogen *burns*, but it does not *support combustion*. It is not very active chemically. Hydrogen is a good *reducing agent*.

*Reduction is the process of abstracting oxygen from a compound*. It is an opposite process to that of oxidation, and both always occur simultaneously.

In the replacement series, the metals have been so arranged that any metal that stands above another in the table will replace that metal from its compounds. The metals at the top of the table are most active.

The hottest flame man has ever produced is made by splitting hydrogen molecules into atoms and utilizing the heat liberated as the atoms recombine. The atomic-hydrogen arc gives a temperature of about 4000° C.

Hydrogen finds use as a *fuel*, as a *reducing agent*, for *filling balloons*, in *making hydrogen compounds*, and in the *hydrogenation of oils*.

## QUESTIONS

## GROUP A

1. What precautions should be taken in preparing hydrogen by the usual laboratory method?
2. Would you expect to find hydrogen present in the free state in the air? Give a reason for your answer.
3. Is hydrogen gas a good fuel? Explain. Is it suitable for illuminating purposes?
4. Carbon monoxide burns with a pale-blue flame. Describe, therefore, a method for making a decisive test for hydrogen.
5. Should bottles of hydrogen be kept mouth upward or mouth downward? Explain.
6. Would you use water or sand to extinguish burning potassium? Explain.
7. Explain why helium is now being substituted for hydrogen for filling dirigibles.
8. Give two reasons why neither sodium nor potassium is suitable for preparing hydrogen in quantity.
9. What would be the effect of lighting the hydrogen at the end of the delivery tube before all the air had been driven out of a hydrogen generator?
10. Explain why reduction cannot take place without oxidation.
11. From the replacement series, pick out at least four metals that could be used instead of zinc for preparing hydrogen. Select three that could not be so used.
12. In the preparation of hydrogen by the use of zinc and sulfuric acid, does the hydrogen come from the zinc or from the acid? Explain.
13. Compare the formulas for *oxides* and *hydroxides* and state clearly the essential differences between them.
14. What would happen if a blazing splint were thrust into: (a) a bottle of hydrogen? (b) a bottle of oxygen? (c) a bottle of hydrogen mixed with oxygen? (d) a bottle of air mixed with hydrogen? How would the reactions differ in the cases of the latter two?
15. In what way does heavy hydrogen differ from ordinary hydrogen? Why is it important?

## GROUP B

16. If you wished to prepare hydrogen in quantity, would you use iron or zinc? Give a reason for your answer.

17. Explain what is meant by saying that zinc is added to muriatic acid to "kill" the acid.

18. If you put a silver teaspoon in a solution of some compound of zinc, what would you expect to happen? What would happen if a bar of zinc were placed in a solution of some silver compound?

19. If there is a blast lamp in your laboratory, compare its construction with that of the oxy-hydrogen blowpipe. How are they alike?

20. Why is reduction so important as a chemical process?

21. Could pure hydrogen be used in your laboratory burner or in the burner of your gas range? Why?

22. From a study of the replacement series, which metals do you think would be most likely to corrode, or tarnish?

23. Write the word equation for the reduction of tin oxide with hydrogen. Label the following: (a) oxidizing agent; (b) reducing agent; (c) substance that is oxidized; (d) substance that is reduced.

## PROBLEMS

1. Sulfuric acid is 2.04% hydrogen. How many grams of hydrogen can be prepared from 50 gm. of sulfuric acid?

2. How many liters would the hydrogen gas from Prob. 1 occupy at S. T. P.? How many cubic meters?

## SUPPLEMENTARY PROJECTS

Prepare a report on the life and work of Henry Cavendish.

Reference: *Encyclopedia Britannica*.

Be prepared to give an account of Langmuir's contributions to theoretical and practical chemistry.

Reference: *Science*. Feb. 24, 1928; Nov. 20, 1925.

Write a paper on the hydrogenation of oils.

Reference: *Scientific American Supplement*. See *Reader's Guide*.

## CHAPTER 6

### THE GAS LAWS

#### Vocabulary

**Direct proportion.** The relation between two factors in which as one increases, the other increases correspondingly.

**Inverse proportion.** The relation between two factors in which as one factor increases, the other shows a corresponding decrease.

**Density.** The weight per unit volume; the weight in pounds per cubic foot, or in grams per cubic centimeter.

**Barometer** (*baros*, "heavy"; *meter*, "measure"). An instrument used to determine the pressure of the air.

**Pressure.** A push or a pull.

**Coefficient.** A number or factor placed before a quantity to show how that quantity is affected by some change; for example, by temperature.

**56. Gas Volumes Vary.** It is true that even solids and liquids do change their volumes and dimensions with a change of temperature and pressure. Such changes are so small that they become negligible, except in cases where precise measurement is required. In dealing with gas volumes, it is *always essential* to consider the effect of both temperature and pressure, for one liter of gas will expand almost four c.c. if warmed only  $1^{\circ}\text{C}.$ , and it will contract almost 13 c.c. if the pressure at sea level is increased 1 cm. of mercury.

Because of such variation, it is necessary to have a standard temperature and a standard pressure at which gases are measured. *The standard temperature used is  $0^{\circ}\text{C}.$ , the temperature of melting ice. The standard pressure used is the weight of a column of mercury 760 mm. high.* This is equal to a pressure of 1034 gm. per sq. cm., or 14.7 lb. per sq. in.

**57. Why 760 mm. Was Selected.** Everyone knows that it is possible to suck soda water through a straw, but not

everyone knows why the soda water rises in the straw. The ancients used to say "Nature abhors a vacuum." Thus they reasoned that when the air was removed from the straw, a vacuum would be produced, and nature would fill it with liquid. But the Duke of Tuscany had a deep well dug, and he found that in the best vacuum he could produce with a pump, water would not rise more than 32 ft. He went to Galileo, an Italian philosopher, for an explanation. He answered, "Evidently nature's horror of a vacuum does not extend beyond 32 ft." It is not certain that Galileo knew the correct answer, and his death occurred before the problem was solved. His pupil, Torricelli, reasoned that mercury, which is a little

more than 13 times as heavy as water, should rise only  $\frac{1}{13}$  as high, or about 30 in., in an exhausted tube.

Therefore he took a glass tube about 36 in. long, closed at one end, filled it with mercury, and inverted it in a bowl of mercury. (See Fig. 55.) Just as he suspected, part of the mercury flowed out of the tube, but *the air pressure on the surface of the mercury in the bowl exerted just enough pressure to balance the mercury column*

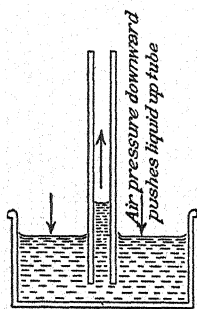


FIG. 56. — Air pressure causes rise of liquids in exhausted tubes.

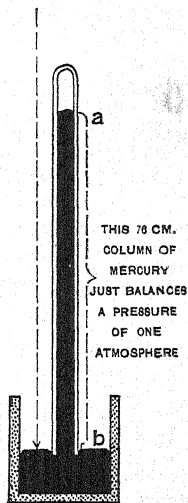


FIG. 55. — Simple barometer.

30 in. high in the tube. Thirty inches is equal to 760 mm., or 76 cm. Thus Torricelli proved that the pressure of the surrounding air is responsible for the rise of liquids in exhausted tubes. (See Fig. 56.) When the air pressure increases, more mercury is pushed up the tube. Part of the mercury

flows out when the air pressure is reduced. The average pressure at sea level is just sufficient to balance a column of mercury 760 mm. high. For that reason "760 mm. of mercury" was chosen as *standard pressure*. Since we live at the bottom

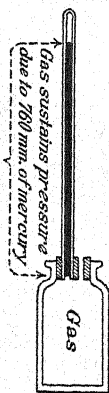


FIG. 57. — The gas is under a pressure equal to that of one atmosphere.

of an ocean of air we are under a pressure equal to 760 mm. of mercury, or 34 ft. of water. We can see just how absurd the old idea was if we try to picture a vacuum (nothing) pulling something up an exhausted tube.

**58. The Barometer.** A simple barometer consists of a Torricellian tube which has been fitted with a graduated scale so that the height of the mercury can be easily measured. Of course the height of the mercury column will vary as the pressure of the air changes slightly from day to day. The student must remember as he works with gases in the laboratory that a bottle of gas is at all times under pressure due to the atmosphere. Figure 57 shows that a bottle of gas standing on the laboratory desk really sustains a pressure equivalent to that of the air pressure. For exact measurement at a given time one has merely to read the barometer.

**59. How a Change in Pressure Affects Gas Volumes.** Everyone knows that a rubber ball filled with air may easily be reduced in volume by squeezing or by pressure. Gases are very elastic, or "springy." If we increase the pressure, the volume decreases, if the pressure is reduced, the gas expands.

Robert Boyle, in experimenting with gases, was the first to make careful measurements to show the mathematical relationship between pressure and volume. (See Fig. 58.) He found, for example, that 1000 c.c. of gas under a pressure of 760 mm. of mercury would have its volume reduced to just one-half if the pressure upon it were doubled. Tripling

the pressure reduces the volume to one-third the original volume. Boyle formulated the results of his experiments on what he called "the spring of the air" in a law that bears his name. **BOYLE'S LAW:** *If the temperature remains constant, the volume of a confined dry gas is inversely proportional to the pressure it sustains.*

Suppose we collect 200 c.c. of an insoluble gas over water as shown in Fig. 59, on a day when the barometer reads 740 mm. We may let the graduated tube of gas stand until the next day. The barometer then reads 760 mm. What will have happened to the gas in the tube? It will have shrunk to  $\frac{740}{760}$  of its former volume, or to a little less than 195 c.c. If we let it stand another day, the barometer may have dropped to 720 mm. The gas will have expanded by  $\frac{740}{720}$ ; its new volume will be more than 205 c.c.

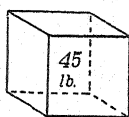
**PROBLEM.** Given 500 c.c. of gas collected when the pressure is 800 mm. What volume will the gas occupy at standard pressure, 760 mm.?

**SOLUTION.** We note that the pressure has been decreased. Therefore, the volume will be increased. We must multiply

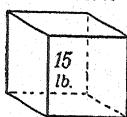
nt locating the curve is nearer to  
".

's Law problems by analysis, as section, the formula  $VP = V'P'$  present the original volume and  $P'$  represent the new volume giving the same problem by sub-

1 cu. ft. Wood



1 cu. ft. Cork



r weight per unit volume, varies.

ve get the equation,  $500 \times 800$

ensity? Suppose we have given cu. ft. of each of the following:

If we weigh each one in turn, are decidedly different. (See and heavy; cork is exceptionally volume of a substance is called its chosen for the English system is expanded by  $\frac{740}{720}$ ; its new volume will be more than 205 c.c.





coordinates in turn, we locate the other points of the curve. By tracing a smooth line through all these points, we have a *curve of inverse proportion*. In all cases, we find that  $VP = \text{a constant}$ . A little practice makes it easy to interpret laws from curves. For example, we observe that as the pressure is increased the point locating the curve is nearer to  $XX'$ , but farther from  $YY'$ .

Instead of solving Boyle's Law problems by analysis, as exemplified in the preceding section, the formula  $VP = V'P'$  may be used.  $V$  and  $P$  represent the original volume and pressure respectively;  $V'$  and  $P'$  represent the new volume and the new pressure. Solving the same problem by sub-

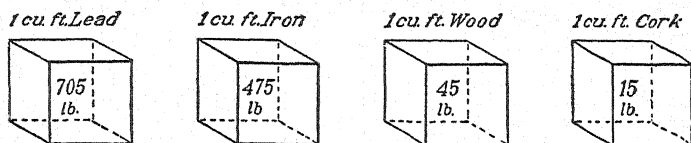


FIG. 61. — The density, or weight per unit volume, varies.

stituting in the formula, we get the equation,  $500 \times 800 = V' \times 760$ .

**61. What Is Meant by Density?** Suppose we have given blocks containing exactly 1 cu. ft. of each of the following: lead, iron, wood, and cork. If we weigh each one in turn, we find that the weights are decidedly different. (See Fig. 61.) Lead is dense and heavy; cork is exceptionally light. *The weight of unit volume of a substance is called its density.* The unit volume chosen for the English system is usually 1 cu. ft.; in the Metric system, it is 1 c.c. Hence, density is expressed in *lb. per cu. ft.*, or in *gm. per c.c.* If we use the letter  $D$  to represent density and the letters  $W$  and  $V$  to represent weight and volume respectively, then we can find the density by dividing the weight by the volume.

$D = \frac{W}{V}$ . From this formula it is obvious that the den-

sity of a given mass of material will be increased if it is compressed so that its volume is reduced.

**62. How a Change of Pressure Affects the Density.** Suppose we have given 1000 c.c. of oxygen gas measured at standard temperature and pressure. Its weight is 1.43 gm.

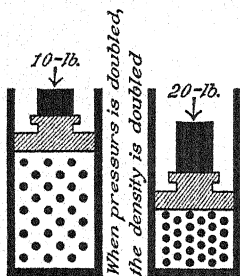


FIG. 62. — Doubling the pressure squeezes the molecules more closely together.

If we compress this gas by doubling the pressure upon it, as shown in Fig. 62, we merely crowd the total number of molecules into one half the space they formerly occupied. Of course the weight is still 1.43 gm., but the *density of the gas has been doubled*. Stated mathematically, *the density of a gas is directly proportional to the pressure it sustains*.

Since an increase in pressure increases the density of a gas, we shall have a greater weight of any gas if we collect 1 liter of it on a day when the barometer reads 760 mm. than we should if the barometer read only 750 mm.

**PROBLEM.** One liter of hydrogen gas at S. T. P. weighs 0.09 gm. Find the weight of 5 liters of hydrogen gas collected on a day when the temperature is standard, but the pressure is 810 mm.

**SOLUTION.** Since the density is *directly* proportional to the pressure, one liter of hydrogen at a pressure of 810 mm. would weigh  $\frac{810}{760}$  times as much as one liter collected at 760 mm. pressure. Hence,  $\frac{810}{760} \times 0.09$  gm. = 0.096 gm. Five liters of the gas at 810 mm. would weigh  $5 \times 0.096$  gm., or 0.48 gm.

**63. How a Change in Temperature Affects Gas Volumes.** Every housewife knows that the heat of the oven will cause the gas set free by the baking powder in biscuits to expand and make the dough rise. The expansion per degree change in temperature is greater for gases than for either solids or liquids. To illustrate, mercury expands nearly 7 times as

much as glass, but any gas will expand nearly 20 times as much as mercury.

Charles, a Frenchman, found that all gases have the same coefficient of expansion. If the pressure does not change, a gas measured at  $0^{\circ}\text{C.}$  will expand  $\frac{1}{273}$  of its volume when heated to  $1^{\circ}\text{C.}$  If heated to  $100^{\circ}\text{C.}$ , its volume would increase  $\frac{100}{273}$  of its former volume. If heated  $273^{\circ}\text{C.}$ , it would expand  $\frac{273}{273}$ , or its volume would be doubled.

If a gas measured at  $0^{\circ}\text{C.}$  be cooled  $1^{\circ}\text{C.}$ , it will contract  $\frac{1}{273}$  of its volume. Cooling to  $-100^{\circ}\text{C.}$  reduces the volume by  $\frac{100}{273}$ . In other words, the gas volume would

C.	A.	Vol.
100	373	373
50	323	323
20	293	293
0	273	273
-100	173	173
-273	0	0

Fig. 63. — Comparison of Absolute and Centigrade Scales.

shrink to  $\frac{173}{273}$  of its original volume. If cooled to  $-273^{\circ}\text{C.}$ , theoretically the gas volume would be reduced to zero. In actual practice, all gases liquefy before that temperature is reached. In 1935, Dr. W. J. de Haas succeeded, by evaporating frozen helium, in reaching a temperature within 0.003 of a degree of absolute zero.

**64. The Absolute Temperature Scale.** Because  $-273^{\circ}\text{C.}$  is believed to be the lowest possible temperature, Sir William Thomson (Lord Kelvin) invented the *absolute scale of temperature*. At  $-273^{\circ}\text{C.}$  molecular motion is believed to cease, and a substance would be absolutely without heat. Thomson used this *absolute zero*,  $-273^{\circ}\text{C.}$ , as the zero on the absolute scale. Figure 63 shows a comparison of the Centigrade and

Absolute scales of temperature, and it also gives the corresponding volumes that a gas, which measures 273 c.c. at  $0^{\circ}\text{C}.$ , will have at the various temperatures shown. For example, at  $20^{\circ}\text{C}.$ , or  $293^{\circ}\text{A}.$ , the volume is 293 c.c. At  $-100^{\circ}\text{C}.$ , or  $173^{\circ}\text{A}.$ , the volume is 173 c.c. *The volumes are directly proportional to the absolute temperatures.*

The LAW OF CHARLES may be stated as follows: *If the pressure is constant, the volume of a dry gas is directly proportional to the ABSOLUTE temperature.* In solving problems, the student must never forget to change Centigrade temperatures to absolute. This is done by *adding 273 to the Centigrade temperature.* For example,  $40^{\circ}\text{C}.$  equals  $313^{\circ}\text{A}.$  ( $40 + 273$ ). Thermometers are not graduated to read absolute temperatures. The absolute scale was devised solely for use in solving problems of this kind. It eliminates the use of *zero* and *minus quantities*. It would be impossible to find volume changes by trying to make a proportion between the temperatures of  $-10^{\circ}\text{C}.$  and  $10^{\circ}\text{C}.$

PROBLEM. Given 500 c.c. of a gas measured when the temperature is  $-10^{\circ}\text{C}.$  What volume will the gas occupy at  $10^{\circ}\text{C}.$ ?

SOLUTION.  $-10^{\circ}\text{C} = 263^{\circ}\text{A}.$ ;  $10^{\circ}\text{C} = 283^{\circ}\text{A}.$  Since the gas was warmed from  $263^{\circ}\text{A}.$  to  $283^{\circ}\text{A}.$ , its volume will expand to  $\frac{283}{263}$  of its original volume.  $\frac{283}{263}$  of 500 c.c. = 538.0 c.c., the new volume.

Or, we may substitute in the following formula:  $V : V' = T : T'$ .  $500 : V' = 263 : 283$ . Whence,  $V' = 538.0$  c.c. Of course  $T$  and  $T'$  represent absolute temperatures.

★ 65. Law of Charles Shown Graphically. Figure 64 shows a *curve of direct proportion* which represents the changes in volume a gas undergoes when heated. The absolute temperatures and volumes shown in Fig. 63 were used as coordinates in plotting this curve. The curve shows clearly that as one factor is increased the other is correspondingly increased.

Suppose we plot the curve  $AB$ , Fig. 65, using the volumes shown in Fig. 63 as abscissas, and the *Centigrade* temperatures as ordinates. If we produce the curve backward it will intersect the  $Y Y'$  axis at  $Z$ , a point equivalent to  $-273^{\circ}\text{C}$ ., or to zero degrees Absolute. This furnishes a graphic illustration of the theoretical temperature at which all gases cease to have volume. A study of the figure also shows why *Absolute* temperatures rather than Centigrade must be used in solving problems involving the use of the law of Charles.

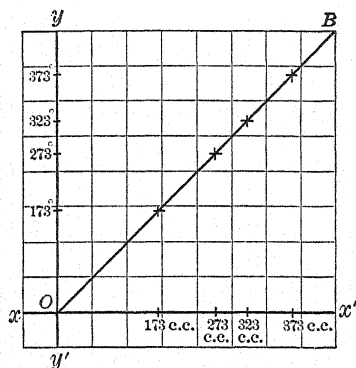


FIG. 64. — Curve to represent law of Charles.

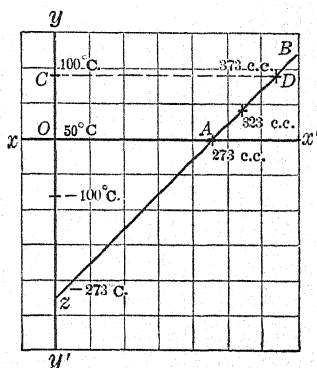


FIG. 65. — Curve to show absolute zero.

In the similar triangles  $ZCD$  and  $ZOA$ , we observe that  $OZ : CZ = OA : CD$ . Therefore  $OA$  and  $CD$ , the corresponding volumes, are proportional to  $OZ$  and  $CZ$ , the *Absolute* temperatures. They are *not* proportional to the Centigrade temperatures.

**66. Correction of Volumes When Both Temperature and Pressure Change.** Problems involving both temperature and pressure changes are very common. In solving such problems, it is possible to find the effect of pressure alone and then use that volume to find the effect of temperature. It is even simpler to combine both changes in one mathematical statement.

**PROBLEM.** Given 500 c.c. of gas measured at 20° C. and 750 mm. pressure. Find what volume the gas will occupy at 30° C. and 760 mm. pressure.

**SOLUTION.** 20° C. = 293° A.; 30° C. = 303° A.

Then,  $500 \times \frac{303}{293}$  = the volume corrected for temperature only.

And,  $500 \times \frac{750}{760}$  = the volume corrected for pressure only.

Since both the temperature change and the pressure change occur simultaneously, we may combine the equations as follows:

$$500 \times \frac{303}{293} \times \frac{750}{760} = \text{corrected volume.}$$

**NOTE.** The increase in temperature from 20° C. to 30° C. causes the gas to expand to  $\frac{303}{293}$  of its volume, and the increase in pressure reduces its volume by  $\frac{750}{760}$ .

The following formula may be used in solving problems of this type:  $\frac{PV}{T} = \frac{P'V'}{T'}$ . In this formula,  $P$ ,  $V$ , and  $T$  represent the original pressure, volume, and absolute temperature, respectively;  $P'$ ,  $V'$ , and  $T'$  represent the new pressure, volume, and absolute temperature.

**PROBLEM.** Calculate the weight of one liter of oxygen measured at a temperature of 27° C. and at a pressure of 750 mm., if one liter of oxygen at S. T. P. weighs 1.43 gm.

**SOLUTION.** The new temperature is higher and the new pressure is lower than standard temperature and pressure. Both these changes would increase the volume, one by  $\frac{300}{273}$ , and the other by  $\frac{760}{750}$ . But an increase in volume decreases the density (weight per unit volume). Therefore we multiply 1.43 gm. by  $\frac{273}{300}$  by  $\frac{750}{760}$  to find the weight of one liter. The result is 1.28 gm.

**67. Factors that Necessitate a Correction in the Barometer Reading.** Sometimes it is impossible to adjust the level of the water line in the gas measuring bottle to correspond with the level of the water in the pneumatic trough. Then, too, when gases are collected over water, some water will evaporate and remain mixed with the gas. Of course this water vapor exerts pressure, and the barometer reading does not show the true pressure which the *dry* gas sustains.



The calculations needed to make such barometer corrections are given in the Appendix.

### SUMMARY

Gases *expand* when heated and *contract* upon cooling. This is also true with most liquids and solids, but the amount of expansion or contraction for a given temperature change is less than for gases. The *standard temperature* for measuring gases is  $0^{\circ}\text{C}.$ ; the *standard pressure* is equal to 760 mm. of mercury. This is equal to about 14.7 lb. per sq. in.

Liquids rise in exhausted tubes because the pressure of the air on the surface of the liquid surrounding the tube pushes the liquid up the tube. The amount of such air pressure is measured by the *barometer*. It is equal to 760 mm. of mercury at sea level, a pressure great enough to balance a column of water 34 ft. high.

The volume of a dry gas is *inversely* proportional to the pressure it sustains. This statement is known as the Law of Boyle, which may be stated algebraically as follows:  $VP = V'P'$ , or  $VP = a \text{ constant}$ .

Charles found that the volume of a gas is *directly* proportional to the *absolute* temperature. The law may be stated as follows:  $V : V' = T : T'$ .

The following formula may be used to find the volume of a gas when both the temperature and pressure change:  $\frac{VP}{T} = \frac{V'P'}{T'}$ .

This expression is often called the "Gas Law."

To convert Centigrade temperatures to Absolute temperatures, add 273 to the observed temperature on the Centigrade scale.

### QUESTIONS

1. What causes liquids to rise in exhausted tubes?
2. In stating Boyle's Law, why is it necessary to speak of the "dry" gas?
3. Name as many applications of Boyle's Law as you can that you have observed in every-day life.
4. Do you think it is possible for the temperature and the

pressure to increase in such a way that the volume of a given mass of gas would neither increase nor decrease? Explain.

5. What is meant by the expression "pressure of one atmosphere"? State its equivalent in: (a) lb. per sq. in.; (b) gm. per sq. cm.; (c) mm. of mercury; (d) ft. of water.

6. Explain exactly what is meant by saying that oxygen is denser than air.

7. Is it desirable, from the viewpoint of the consumer, to have the gas meter in the basement or in the attic? To have the gas meter in a warm place or a cool one?

8. An automobile tire is inflated to 35 lb. pressure on a cool morning. Will the tire show a higher or lower pressure after it has stood in the sun for a few hours?

## PROBLEMS

### GROUP A

1. A gas collected when the pressure is 820 mm. has a volume of 2000 c.c. Find its volume at standard pressure.

2. A gas has a volume of 100 c.c. when the pressure is 65 cm. What pressure will be needed to reduce the gas volume to 60 c.c.?

3. A liter vessel was filled with gas when the barometer read 780 mm. What will be the new volume of the gas if the pressure is increased 20 mm.?

4. Given 88 c.c. of hydrogen gas at  $21^{\circ}\text{C}$ . Find its volume at  $42^{\circ}\text{C}$ .

5. A gas measures 150 c.c. at a temperature of  $-10^{\circ}\text{C}$ . Find its volume at  $10^{\circ}\text{C}$ . (The student may be interested in trying to solve this problem by using Centigrade temperatures. Is the result reasonable?)

6. A gas has a volume of 180 c.c. when the temperature is  $45^{\circ}\text{C}$ . What temperature is needed to reduce the volume of the gas to 120 c.c.?

7. Reduce to standard conditions: 1200 c.c. of gas at  $30^{\circ}\text{C}$ . and 800 mm. pressure.

8. Reduce to standard conditions: 1500 c.c. of gas at  $-20^{\circ}\text{C}$ . and 700 mm. pressure.

9. Reduce to standard conditions: 800 c.c. of gas at  $-30^{\circ}\text{C}$ . and 780 mm. pressure.

10. Given 100 c.c. of gas measured at  $0^{\circ}\text{C}$ . and 380 mm. pressure. What will be the volume at  $273^{\circ}\text{C}$ . and 760 mm. pressure?

11. A gas collected when the temperature is  $18^{\circ}\text{C}$ . and the pressure is 810 mm. measures 450 c.c. Find its volume the next day when the thermometer reads  $24^{\circ}\text{C}$ . and the barometer reads 745 mm.

## GROUP B

12. A gas measures 250 c.c. when the temperature is  $27^{\circ}\text{C}$ . and the pressure is 775 mm. If the temperature is increased to  $36^{\circ}\text{C}$ ., what pressure must be used to keep the gas at the same volume?

13. One liter of oxygen weighs 1.43 gm. at S. T. P. Find the weight of one liter of oxygen when the temperature is  $21^{\circ}\text{C}$ . and the pressure is 720 mm.

14. Two hundred and twenty-five c.c. of gas weigh 4.5 gm. when the temperature is  $15^{\circ}\text{C}$ . and the pressure is 78 cm. of mercury. Find the weight of 22.4 liters of this gas at S. T. P.

15. A man has his gas meter in the basement, where the average pressure is 75 cm. of mercury. If he uses 2000 cu. ft. per month, how many cu. ft. would he need to use per month to get the same heat value, if he moved the meter to the attic where the average pressure is 74.5 cm.?

16. A baker kneads 60 cu. in. of air into the dough for a loaf of bread at room temperature,  $20^{\circ}\text{C}$ . Assuming that 10% of the gas escapes during the baking, how many cubic inches of bread will be formed, if the oven temperature is  $167^{\circ}\text{C}$ .?

17. A toy balloon has a volume of 1500 c.c. when it is filled with hydrogen at a temperature of  $17^{\circ}\text{C}$ ., and it sustains a pressure of 750 mm. It rises to a height where the temperature is  $-23^{\circ}\text{C}$ . and the pressure is 300 mm. Calculate the volume of the balloon under the new conditions.

18. A cylinder of gas holding 3 cu. ft. is filled when the temperature is  $17^{\circ}\text{C}$ . and the pressure used in filling is 40 atmospheres. The cylinder bursts in a room where the temperature is  $27^{\circ}\text{C}$ ., and the pressure is one atmosphere. To what volume will the gas expand?

19. A room is heated from  $0^{\circ}\text{C.}$  to  $20^{\circ}\text{C.}$  What fractional part of the air escapes? If the density of the air at  $0^{\circ}\text{C.}$  was 0.00128 gm. per c.c., what will be its density at  $20^{\circ}\text{C.}$ ?

20. A gas measures 400 c.c. at a temperature of  $25^{\circ}\text{C.}$  and a pressure of 800 mm. To what temperature must the gas be cooled if its volume is reduced to 350 c.c. when the pressure is 760 mm.?

### SUPPLEMENTARY PROJECTS

Prepare a report on the life and work of Robert Boyle or of Jacques Charles.

Reference: *Encyclopedia Britannica*.

Give an account of Galilei Galileo's contributions to science.

References: HART, I. B., *Makers of Science*. Oxford University Press.

PHILLIPS, M., AND GEISLER, W. H., *Glimpses into the World of Science*. Heath.

Low Temperature. See *Reader's Guide*.

## CHAPTER 7

# WATER AND HYDROGEN PEROXIDE

### Vocabulary

**Calorie.** The unit used in the Metric system for measuring heat.

**Stable.** Not easily decomposed, as applied to compounds.

**Hydrate.** A compound that contains water in its constitution.

**Hydrolysis.** The decomposition of a compound by the action of water.

**Anhydrous.** Without water.

**Dehydration.** The process of removing water from a substance.

**Multiple.** A number that exactly contains another number.

### A. WATER

**68. Water — the Most Abundant Compound.** Water is not only one of our most abundant compounds, but it is also one of the most useful. We find water in the air in the form of water vapor. About three-fourths of the earth's surface is covered with water. Many of our foods, such as tomatoes, cabbage, watermelon, celery, cucumbers, etc., contain 90% or more of water. Some of our foods that seem fairly dry contain 50% or more of water by weight. For example, bread is a little less and meat a little more than 50% water. The majority of our vegetables contain at least 75%, and milk contains about 88%. Our physiologies tell us that a man who weighs 140 lb. is composed of about 100 lb. of water by weight.

**69. Physical Properties of Water.** Pure water is odorless and tasteless. Any odor or taste in drinking water is due to impurities dissolved in the water, either mineral matter, carbon dioxide, or other gases. The taste and odor of the water from some mineral springs is due to the presence of

such substances in considerable quantity. In thin layers water is colorless; deeper layers have a blue color, or a faint "bluish tint."

At ordinary temperatures water is a liquid; it changes to ice at  $0^{\circ}\text{C.}$ , or  $32^{\circ}\text{F.}$  As water solidifies, it expands slightly. The bursting of water pipes when they freeze is a common example that shows the force of such expansion. Ice has a density about 0.9 as great as that of water. One cu. ft. of water weighs 62.4 lb., but one cu. ft. of ice weighs only a trifle more than 57 lb. *One cubic centimeter of water, at  $4^{\circ}\text{C.}$ , weighs one gram.*

Under a pressure of one atmosphere (760 mm. of mercury), water boils at  $100^{\circ}\text{C.}$ , or  $212^{\circ}\text{F.}$  The steam that is formed when one liter of water evaporates occupies about 1700 liters. A small quantity of water in our furnace supplies enough steam to fill the pipes and radiators all over the house. It is this expansive force that water exerts when it evaporates that gives steam its ability to run steam engines. If we reduce the atmospheric pressure upon the water surface, water boils at a temperature *below*  $100^{\circ}\text{C.}$  At the city of Quito, Ecuador, 9000 ft. above sea-level, water boils at about  $90^{\circ}\text{C.}$  If we lower the pressure to about 47 mm. of mercury, water then boils at  $37^{\circ}\text{C.}$ , or at body temperature ( $98.6^{\circ}\text{F.}$ ). All liquids boil at a lower temperature under reduced pressure. They also evaporate much faster in a partial vacuum. In the industries, vacuum pans are extensively used to facilitate rapid drying at moderate temperatures. In making condensed milk, or in making powdered milk, the water in the normal milk is evaporated in a partial vacuum to increase the speed of evaporation and to prevent scorching the solids in the milk. (See Fig. 66.)

**70. Water Is Used as a Standard.** Water is very abundant and it is quite easy to obtain water in a fairly pure condition. Hence it is used as a standard in *graduating thermometers* and in *specific heat* and *specific weight* determina-

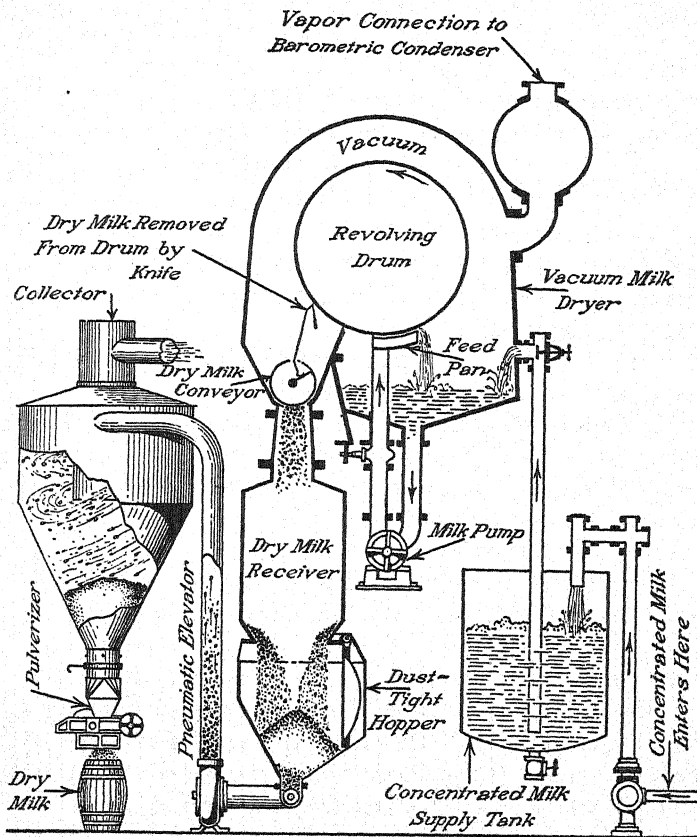


FIG. 66. — After part of the water from the milk has been evaporated, it enters a chamber which is kept under reduced pressure. As the milk solids collect on a rotating drum, they are scraped off and conveyed to barrels or other containers.

tions. When we use the term “specific” in physics or chemistry, we imply a ratio or comparison. For example, the *specific weight*, or *specific gravity*, of a substance is that number which tells us how many times as heavy that substance is as the same volume of water. For example, *one c.c.*



of water at 4° C., the temperature at which water is most dense, *weighs exactly one gram*. One c.c. of mercury weighs 13.6 gm. Therefore, mercury is 13.6 times as heavy as the same volume of water. The specific weight of mercury is

13.6. Specific weight =  $\frac{\text{density of substance}}{\text{density of water}}$ . Water is used

as the standard for specific weight determinations for all solids and liquids. It is not satisfactory for determining the specific weights of gases. Either *air* or *hydrogen* is used as the standard for gases.

Water heats slowly and it cools slowly. The climate in San Francisco is not subject to such great extremes of temperature as that of St. Louis. The water of the Pacific Ocean, warming slowly and cooling slowly, exerts a moderating influence upon the climate of those cities on the Pacific Coast. We measure heat in *calories*. *It takes one calorie of heat to raise the temperature of one gram of water one degree Centigrade*. One calorie of heat is lost when one gram of water cools through one degree Centigrade. It takes one British Thermal Unit (Btu) of heat to warm one pound of water one degree Fahrenheit. The number of calories needed to raise the temperature of 1 gm. of any substance 1° C. compared to the number of calories needed to raise the temperature of 1 gm. of water 1° C. is the *specific heat* of that substance. For example, it takes only  $\frac{1}{8}$  as many calories to warm a mass of iron 1° C. as it does to warm the same weight of water 1° C. Iron has a specific heat of only 0.112.

**71. Water Is the Best General Solvent.** In the laboratory we use many of our chemicals in solution. In nearly all cases water is used as the solvent. In fact, water will dissolve more different substances than any other chemical. We ordinarily consider that the dissolving of a substance in water is a *physical property*. In some cases, a *chemical* action doubtless occurs when the substance dissolves in water. There are no words in the English language to distinguish between

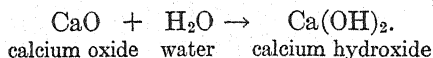
*physical solution* and *chemical solution*. Hence the term *dissolve* is often loosely used.

**72. Chemical Properties of Water.** 1. *Stability.* We learned that Priestley split up mercuric oxide into mercury and oxygen by focusing the sun's heat upon the compound. We call mercuric oxide an *unstable* compound, because it is not difficult to decompose it. We might expect water, a compound of hydrogen and oxygen, to behave in a similar manner. But unfortunately we cannot draw such conclusions in chemistry, and expect that because one oxide decomposes easily all other oxides will do the same. In fact, water is so *stable* that less than 2% is decomposed at the very high temperature of 2000° C. When some elements combine chemically, tremendous quantities of heat energy are set free. (See Table 8 in the Appendix.) Such elements often unite with explosive violence. It takes a tremendous amount of energy of some type to decompose such compounds. Elements that combine easily generally form stable compounds; those that are hard to combine generally form compounds that are unstable.

2. *Action with metals.* In the preparation of hydrogen we learned that sodium, potassium, and calcium will decompose *cold* water. Magnesium decomposes *boiling* water, and such metals as iron, aluminum, and zinc interact with water when the metals are heated to a *red heat*.

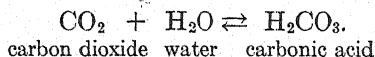
3. *Action with the oxides of metals.* When metals are burned in air or oxygen, metallic oxides are formed. Many such oxides are insoluble in water, and they do not interact with water at all. Some of the active metals (see Replacement Series, page 76) form oxides that unite with water chemically and form *hydroxides*. We have already learned that sodium hydroxide in water solution acts like a *base* and has properties quite the opposite to the properties of acids. Such reaction is typical of the behavior of the soluble hydroxides. Every student has probably seen a mason slaking

lime, although much of this work is now done at the plant where lime is manufactured. Quicklime is *calcium oxide*,  $\text{CaO}$ . When it is added to water, the following chemical reaction takes place:



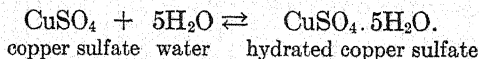
The quicklime unites with the water chemically with the evolution of much heat. Metallic hydroxides are known to chemists as *bases*. The soluble active bases are called *alkalis*.

4. *Action with the oxides of non-metals.* When we burn carbon in air, carbon dioxide is formed. This gas will unite with water to form a compound known as *carbonic acid*. The equation follows:



This reaction is typical of the behavior of the oxides of non-metals. For example, the oxides of sulfur, phosphorus, and nitrogen unite chemically with water to form *acids*.

5. *Hydrates.* Many compounds dissolve in water. As the water evaporates, crystals of such compounds are formed. *Copper sulfate*, or blue vitriol, for example, separates from such a water solution in the form of beautiful blue crystals that have the formula  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The period here does not mean "multiplied by," but it indicates that five molecules of water have in some way rather loosely combined with one molecule of copper sulfate as it crystallized.



The double arrows indicate that the reaction is reversible. For example, heating *hydrated* copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) to about  $100^\circ \text{C}$ . drives off all the water and leaves *anhydrous* copper sulfate ( $\text{CuSO}_4$ ). The word *hydrate* means that the compound contains water; *anhydrous* means without water;

the processes are called *hydration* and *dehydration* respectively.

6. *Water brings about chemical changes and acts as a catalyst.* When water is added to baking powder a gas is evolved and chemical action begins immediately. In many cases no action between chemicals is apparent in the *dry* state. As soon as water is added, the action begins. The water appears to act as a general catalyst. In fact, some chemists maintain that a trace of moisture is a requisite for chemical action. Experiments have shown that perfectly dry hydrogen and oxygen do not explode when mixed and ignited.

**72a. Heavy Water.** When heavy hydrogen unites with oxygen, the water that is formed is about 1.1 times as dense as ordinary water. Heavy water freezes at  $3.82^{\circ}\text{C}.$ , and boils at  $101.45^{\circ}\text{C}.$  It is present in water in the ratio of about 1 to 5000. Dr. Taylor finds that it is toxic enough to kill tadpoles in about one hour.

**73. Composition of Water by Volume.** Under the preparation of hydrogen and oxygen, we learned that water may be decomposed by means of the electric current. If we collect both gases by the use of an apparatus like that shown in Fig. 17, we shall find that *2 volumes of hydrogen* are liberated to *1 volume of oxygen*. The analysis of water always yields these elements in the same proportion by volume.

Further proof that water is composed of hydrogen and oxygen in the proportion of two to one may be had by re-

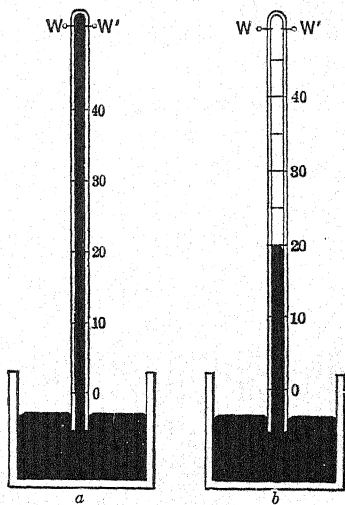
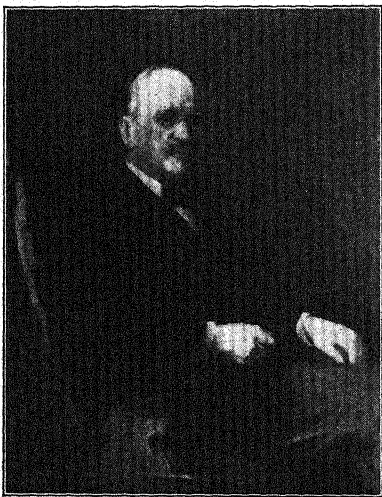


FIG. 67. — Eudiometer tube for measuring gases.

combining these elements to form water. Figure 67a shows a eudiometer tube arranged for collecting gases by mercury displacement.

Suppose we introduce 20 c.c. of hydrogen and 10 c.c. of oxygen into the tube as shown in Fig. 67b, and pass an electric spark between the wires  $w$  and  $w'$ . The mixture explodes and water vapor is formed. As the vapor condenses, the mercury rises in the tube. No hydrogen or oxygen is left uncombined. If we start with 20 c.c.



Courtesy Western Reserve Univ.

FIG. 68. — Edward Morley (1838–1923) was born in Newark, N.J. At Western Reserve University, where he was Head of the Department of Chemistry, he performed his experiments on the composition of water.

of hydrogen and 20 c.c. of oxygen, the explosion takes place as before, but 10 c.c. of oxygen are left uncombined. If we use 30 c.c. of hydrogen and 10 c.c. of oxygen, then we have 10 c.c. of hydrogen remaining uncombined. All attempts to make hydrogen and oxygen combine directly in any other ratio by volume than 2 to 1 result in failure.

Thus it has been proven by both *analysis* and *synthesis* that, if all have the same temperature and pressure, *two volumes of hydrogen + one volume of oxygen → two volumes of water vapor*.

**74. Composition of Water by Weight.** An American chemist, Edward William Morley, is well known for his very accurate work in determining the composition of water by weight. (See Fig. 68.) He weighed the hydrogen and the oxygen, and then the water that was produced by their

union. As a result of his experiments, he found that one part by weight of hydrogen combines with 7.94 parts by weight of oxygen to form 8.94 parts by weight of water. To weigh gases in a vacuum at standard conditions of temperature and pressure involves such refinement of apparatus and such careful manipulation that some indirect method of finding the composition of water by weight is more often used. The following method was devised by Jean Dumas, a French chemist.

A weighed quantity of copper oxide is placed in a hard glass tube, as shown in Fig. 69. Dry hydrogen is then passed over the *heated* oxide; it reduces the copper oxide to metallic

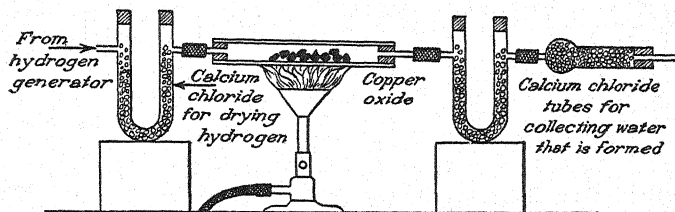


FIG. 69. — Composition of water by weight.

copper, and unites with the oxygen to form water. The water thus formed is absorbed in a previously weighed tube containing granular calcium chloride. The copper oxide tube shows a loss of weight due to the abstraction of oxygen. The calcium chloride tube shows an increase in weight due to the absorption of water. Suppose we start with 23.8 gm. of copper oxide. After heating, it weighs 15.86 gm. The loss of weight, 7.94 gm., is the weight of the oxygen used to form water. The calcium chloride tube weighed 80 gm. before the experiment, and 88.94 gm. after its completion. The gain in weight, 8.94 gm., is the weight of the water formed:  $7.94 \div 8.94 = 88.81$ , the per cent of oxygen. One gram, the weight of hydrogen which must have combined with the oxygen, divided by 8.94 equals 11.19% hydrogen. There-

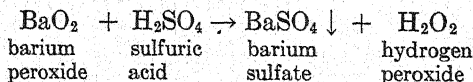
fore, water is made up of 88.81% of oxygen by weight, and 11.19% of hydrogen. It is *approximately* correct to say that 1 gm. of hydrogen combines with 8 gm. of oxygen to form 9 gm. of water.

Here, again, we have found it possible to use both analysis and synthesis to show the composition of water. Hundreds of such analyses have been made, and the result is consistent.

### B. HYDROGEN PEROXIDE

**75. Hydrogen Peroxide,  $H_2O_2$ .** We have learned that we always have *two* atoms of hydrogen combine with *one* atom of oxygen when hydrogen is burned. From a study of the formula for hydrogen peroxide,  $H_2O_2$ , one would suspect that it could be made by oxidizing water. But things are not always what they seem, and when one tries to burn water to form hydrogen peroxide, he always fails. It is possible to form such a compound by *indirect* methods.

**76. How Is Hydrogen Peroxide Prepared?** The prefix "per" means "thoroughly saturated with," as we use it in chemistry. Several peroxides can be prepared quite easily. If barium peroxide,  $BaO_2$ , is treated with a cold dilute solution of sulfuric acid ( $H_2SO_4$ ) in water, a double decomposition reaction occurs. The equation follows:

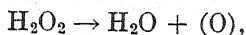


**77. Properties of Hydrogen Peroxide.** Pure hydrogen peroxide is a thick, syrupy liquid, about  $1\frac{1}{2}$  times as dense as water. The pure liquid is unstable, and it may explode violently. For that reason hydrogen peroxide is always sold in dilute water solutions. If such a dilute solution is kept in the dark, it will keep fairly well. Yet it is not uncommon to find the pressure produced by the gas formed as it decomposes sufficient to blow the stopper out of the bottle. One



bottle of a 3% solution will yield 10 bottles of oxygen; hence the expression "10 V." which is so often seen on the label of the bottle.

From the equation,



we see that hydrogen peroxide forms nothing but water and oxygen as it decomposes. Chemists have learned that an element which is just being liberated from a compound is *especially active chemically*. Under such conditions *an element is said to be in its nascent (nasci, "to be born") state*. Some chemists believe that such a *single atom* of oxygen can combine readily with some other substance. If no other substance is present, then two oxygen atoms combine to form a molecule of oxygen,  $\text{O}_2$ . The ability of both ozone ( $\text{O}_3$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to decompose and liberate *nascent oxygen* makes them extremely vigorous oxidizing agents.

**78. Uses of Hydrogen Peroxide.** Oxidizing agents destroy the color of many organic compounds; they also kill bacteria. Hydrogen peroxide finds use in bleaching wool, silk, ivory, hair, and feathers. Its use for cleansing wounds has fallen into disfavor with certain physicians, since they claim that it attacks the tissues and causes the wound to heal more slowly. Either a tincture of *iodine* or a solution of *mercurochrome* is now more commonly recommended for sterilizing surface wounds.

### C. LAW OF MULTIPLE PROPORTIONS

**79. What Is the Law of Multiple Proportions?** It is not at all uncommon to find that the same two elements unite in different proportions to form two or more compounds. The fact that 1 part by weight of hydrogen unites with 7.94 parts by weight of oxygen to form water is an example of the law of *definite* proportions. The fact that 1 part by weight

of hydrogen unites with 15.88 parts by weight of oxygen to form hydrogen peroxide is also an example of the same law. But we need another law or statement to explain the habit that such elements as hydrogen and oxygen have when they unite to form a *series of compounds*.

John Dalton, the same man who formulated the Law of Definite Proportions, studied several series of compounds. Let us tabulate two of them with the approximate weights in which they combine:

H <sub>2</sub> O	1 gm. H and 8 gm. O
H <sub>2</sub> O <sub>2</sub>	1 gm. H and 16 gm. O

CO	12 gm. C and 16 gm. O
CO <sub>2</sub>	12 gm. C and 32 gm. O

From these tables we see that in the compounds water (H<sub>2</sub>O) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) the weight of hydrogen is *fixed* or *constant*, and the weights of oxygen, 8 and 16, have the simple ratio of 1 to 2. In the second table we observe that in the compounds carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) the weight of carbon is *fixed* or *constant*, and that the weights of oxygen, 16 and 32, have the simple ratio of 1 to 2. The LAW OF MULTIPLE PROPORTIONS may be stated as follows:

*Given two elements that unite to form a series of compounds; the weight of one element, which we may call "A," may be considered fixed. Then the weights of the other element, "B," will be in the ratio of small whole numbers.* This law is known as the Law of *Multiple Proportions*, because the weight of the oxygen in the hydrogen peroxide is 16, a multiple of the weight of oxygen in water, 8. In the second example, 32 is a multiple of 16.

### SUMMARY

Water is the most abundant compound. It is present in the air, the ocean, and in nearly all our foods.

Water is odorless, tasteless, and colorless. It freezes at 0° C.

and boils at  $100^{\circ}\text{C}$ . It is densest at  $4^{\circ}\text{C}$ .; at that temperature 1 c.c. of water weighs 1 gm. One cu. ft. of water weighs 62.4 lb.

Chemically, water is very *stable*. It unites with such *active metals* as sodium and potassium, liberating hydrogen. It combines with the *oxides of metals* and forms *bases*. It combines with the *oxides of non-metals* and forms *acids*. It forms many *hydrates*. It serves as a general catalyst. Dr. Urey was awarded the Nobel prize in 1934 for his research work with *heavy water*.

By *analysis* it has been shown that water is made up of *two volumes of hydrogen to one volume of oxygen*. When these two elements unite in the same ratio, water is formed.

In a classical experiment, noted for its painstaking accuracy, Edward Morley showed that water is composed of *one part by weight of hydrogen to 7.94 parts by weight of oxygen*.

*Hydrogen peroxide* finds use as an oxidizing agent; as a disinfectant; and as a bleaching agent. An element just as it is set free from a compound is said to be in the *nascent state*. It has more energy at that time and is more active.

The Law of Multiple Proportions may be stated: When two elements unite to form a series of compounds, if we consider a fixed weight of one element, "A," then the weights of the other element, "B," will be in the ratio of small whole numbers.

## QUESTIONS

### GROUP A

1. Explain why water is so satisfactory in the "hot-water bottle" for use in sick rooms.
2. Why is it impossible to have pure water in nature?
3. How are the solvent properties of water related to sanitation and cleanliness?
4. Is steam visible? What is the so-called steam that issues from the spout of a teakettle?
5. Why is hydrogen peroxide generally kept in dark-colored bottles?
6. Make a list of the different ways in which we make use of water. Can you think of another compound that is so important?

7. In what ways are "vacuum pans" used in the field of chemistry?

8. What is the difference in meaning between "calorie" and "degree"? Illustrate.

#### GROUP B

9. How would natural conditions be affected if water contracted during solidification?

10. How does water moderate the climate of such a place as Honolulu? Does it produce a similar effect on the climate of Boston? Explain.

11. Would water be of value in putting out a fire if the temperature of the burning substance were  $2500^{\circ}\text{C}.$ ?

12. How would you proceed to determine the per cent of water in a sample of milk?

13. Would water boil more quickly at the top of Pike's Peak or in New York City? In which place would vegetables cook faster? Explain.

14. Why is the research work with heavy water that is being carried on now so very important?

#### PROBLEMS

##### GROUP A

1. Suppose we mix 45 c.c. of hydrogen with 20 c.c. of oxygen and ignite the mixture. What gas remains, and what is its volume?

2. What gas is left after a mixture of 75 c.c. of oxygen and 80 c.c. of hydrogen are ignited? What is its volume?

3. Air is 21% oxygen. Twenty-five liters of air are mixed with 4 liters of hydrogen and the mixture is ignited. How many c.c. of gas are left? What gases will be left?

4. The specific weight of concentrated sulfuric acid is 1.84. If you bought some sulfuric acid and found that it was only 1.6 times as heavy as the same volume of water, what would you infer?

## GROUP B

5. Nitric acid has a specific weight of 1.4. Calculate the weight of one liter of nitric acid.

6. How many grams of water would be formed by burning 23.82 gm. of oxygen in the presence of 8 gm. of hydrogen? How many grams of hydrogen would be left uncombined? Is it correct to speak of burning oxygen in this case?

7. A man has a refrigerator with an ice compartment of the following dimensions: 18" by 15" by 12". How many pounds of ice will it hold?

8. Given 600 c.c. of hydrogen measured at 24° C. and 80 cm. pressure, and 300 c.c. of oxygen measured at - 50° C. and 780 mm. pressure. What gas is left after the mixture is exploded, and what is its volume at S. T. P.?

## SUPPLEMENTARY PROJECTS

Prepare a report on the life and work of Edward Morley and of John Dalton.

References: MOORE, F. J., *History of Chemistry*. McGraw-Hill.  
*Encyclopedia Britannica*.

Heavy Water. See *Reader's Guide*.

## CHAPTER 8

# SOLUTION AND CRYSTALLIZATION

### Vocabulary

**Solubility.** The ratio of the weight of the solute to the weight of the solvent.

**Miscible.** Liquids that are soluble in each other are said to be miscible.

**Effervescence.** The commotion in a liquid produced by the rapid escape of a large number of gas bubbles.

**Efflorescence.** The loss of water by crystals upon exposure to air.

**Deliquescence.** The property some substances have of adsorbing moisture from the air and becoming wet.

**Hygroscopic.** The property some substances have of adsorbing a thin film of moisture on their surfaces.

**Desiccator** (*desiccare*, "to dry up"). An apparatus used in the laboratory to dry chemicals.

### A. SOLUTIONS

**80. Characteristics of a Solution.** One of the most important properties of water is its ability to dissolve certain substances. If we add a little sugar to water, the sugar gradually disappears. It goes into solution in the water, but it does *not melt*, as some incorrectly state. The liquid that is used to bring about solution is called the *solvent*. The substance that goes into solution is called the *solute*. Let us add a small crystal of potassium permanganate to a liter or more of water, and stir the liquid until the crystal has all dissolved. Every drop of this solution will have a reddish-purple tint, thus showing that in solution the particles are finely divided. If we put a drop of the solution under a compound microscope, we cannot see the small particles of the solute.

If we stir our coffee until the sugar is all dissolved, a

spoonful from the top will be just as sweet as one taken from the middle or from the bottom of the cup. When a cold solution stands, the solute does not separate from the solvent.

A solution has the following characteristics: (1) *It is homogeneous*, having the same nature throughout; (2) *The particles of the solute are so very finely divided that they cannot be removed by passing the solution through a filter*; (3) *The solute does not separate from the solvent upon standing unless the temperature changes, or some of the solvent evaporates*. Material *suspended* in a liquid tends to separate upon standing. Thus we see that *a solution is really a uniform mixture consisting of a solvent and the solute*.

The question whether solution is a physical or a chemical change is one upon which chemists are still in doubt. It seems reasonably certain that chemical action occurs in dissolving some compounds. In other cases the action appears to be physical. When water is the solvent, the solute often unites with it to form hydrates. In such a case this part of the action is doubtless chemical, but if the hydrate then dissolves in the excess water that is present, the action is probably physical. It is incorrect to say that metals dissolve in acids. They interact with the acid to form a new compound, which may then dissolve in the excess water which was present in the acid. We always use water solutions of acids instead of pure acids.

**81. Saturated Solutions.** Some substances dissolve easily in water and others are almost *insoluble*. Students are generally surprised to hear one speak of the solubility of glass. Yet it does dissolve to a slight extent, as is true with nearly all substances. But substances that are so slightly soluble are generally classed as *insoluble substances*.

Everyone knows that it is possible to dissolve in a cup of coffee one lump of sugar, two lumps, or even more. Such a solution is not a true compound, or it would be possible



to dissolve a definite amount only. When only one lump is dissolved in a large cup of coffee, the solution is rather *dilute*. As we continue to dissolve more and more sugar, the solution becomes more *concentrated*. If we continue to add more sugar, stirring constantly, we finally reach a point where no more sugar can be dissolved unless we raise the temperature. *When a solvent under such conditions holds all the solute it can, the solution is said to be saturated at that temperature.* It is easier to make a saturated solution by adding to the solvent a considerable *excess* of the solute and then agitating the mixture at a *constant temperature* until all the solute has dissolved that will.

**82. What Is Meant by Solubility?** Actual experiment shows that it is possible to dissolve 35.5 grams of common salt in 100 grams of water at  $0^{\circ}\text{C}$ . Other experiments show that it is possible to dissolve 13.4 gm. of potassium nitrate in 100 grams of water at  $0^{\circ}\text{C}$ ., or to dissolve 3.5 grams of potassium chlorate in the same amount of water. The *solubility* of a substance may be expressed as the number of grams of solute needed to saturate a definite weight of solvent. See Table 4 in Appendix. *Note that the temperature must be specified. The solubility of a substance may be defined as the ratio of the weight of the solute to the weight of solvent, as applied to a saturated solution at a given temperature.*

**83. Solvents and Solutes.** 1. *Solvents.* There are many different kinds of solvents used in chemistry. Water is the best solvent known, since more different substances are more or less soluble in water than in any other solvent. Other well-known solvents include the various alcohols, gasoline, ether, turpentine, and carbon tetrachloride. An alcoholic solution of a non-volatile substance is called a *tincture*. The name *spirits* is given to the alcoholic solution of volatile substances. For example, in pharmacy we have tincture of iodine, an alcoholic solution containing 7% of iodine; *aromatic spirits of ammonia* is an alcoholic solution of ammonia and

a volatile compound of ammonia, with some nutmeg and oil of lemon.

2. *Solutes.* The solute may be a solid, a liquid, or a gas. When two liquids are *mutually* soluble in each other, they are said to be *miscible*. For example, water and alcohol are *miscible* in all proportions. We may also mix glycerine with water in any proportion we choose. It is well known that oily liquids do not mix with water. They are not soluble in each other; they are *immiscible*.

When a small quantity of an oily liquid is vigorously shaken with water, the oil particles become finely divided and remain *temporarily suspended* in the water. Such a suspension of an oily liquid in water is called an *emulsion*. Milk that is freshly drawn from the udder of the cow is a good example of an emulsion. When it stands the fat globules gradually separate from the water and rise to the top of the container. Several substances, known as *emulsifying agents*, are used to make emulsions more permanent. Gums have this property and are much used in making emulsions in pharmacy. In making mayonnaise dressing, egg yolks are used to make the olive oil emulsion more permanent. Greasy dishes are difficult to wash with water alone, because the water and grease do not mix. When soap is added to the water it serves as an emulsifying agent, and the soapy water forms an emulsion with the grease.

We have already learned that air, oxygen, and hydrogen are somewhat soluble in water. Most gases are to some extent soluble in water; in some cases several volumes dissolve in one volume of water. See Table 5 in the Appendix.

#### 84. How a Change in Temperature Affects Solubility.

1. *Of Solids.* The solubility of a solid depends upon three things: (1) The nature of the solid itself; (2) The nature of the solvent; and (3) The temperature. (See Fig. 70.) These curves show us at a glance that *an increase in temperature increases the solubility of a solid*. For example, we find that

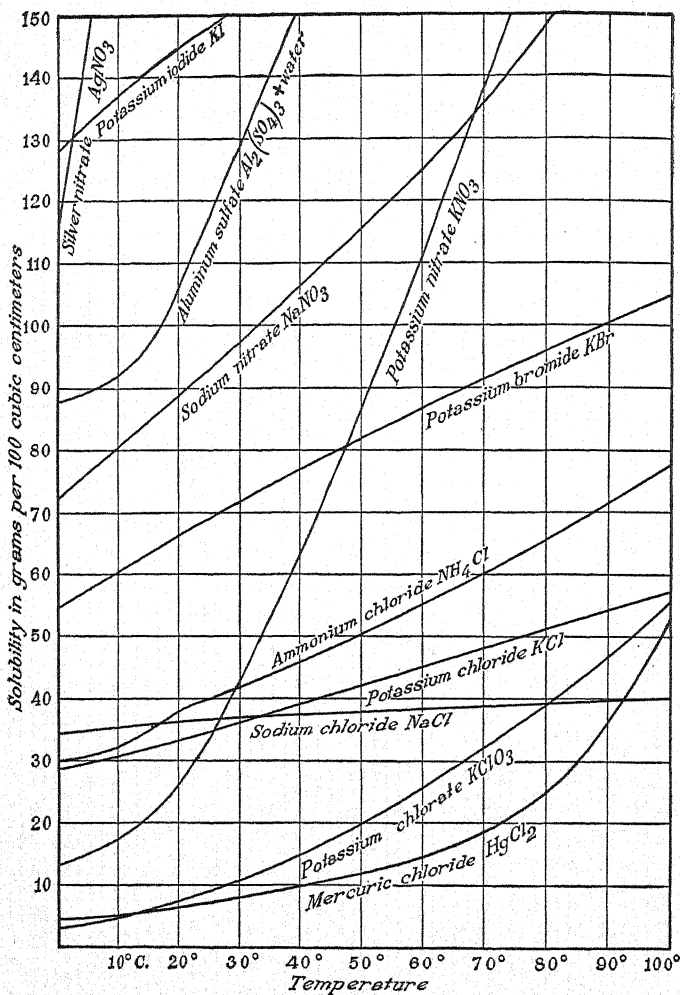


FIG. 70. — These curves show the effect of temperature on the solubility of solids. The student will observe that the solubility of sodium chloride is little affected by an increase in temperature.

only about 13 gm. of potassium nitrate will dissolve in 100 grams of water at  $0^{\circ}\text{C}.$ ; if the water is warmed to  $30^{\circ}\text{C}.$ , 44 gm. will dissolve; at  $70^{\circ}\text{C}.$ , almost 140 gm. of potassium nitrate can be dissolved in only 100 gm. of water. Table 6 in the Appendix shows us that most solids behave in a similar manner, but we note that there are a few exceptions. Calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , and calcium sulfate,  $\text{CaSO}_4$ , are slightly more soluble in cold water than in hot water.

2. *Of liquids.* Liquids mix rather more easily at higher temperatures. They are like solids from the fact that the mutual solubility increases as the temperature increases, until the boiling point of one of the liquids is reached.

3. *Of gases.* A glass of water drawn from the hot water tap often appears milky. As it stands, bubbles of gas (air) can be seen rising through the water. The air which was dissolved by the cold water has been driven out of solution by the heating of the water. This proves that air is *less soluble* in hot water than in cold. Other gases behave in the same manner. Their *solubility decreases as the temperature increases*. Boiling the liquid drives out of solution, or expels, all the gas that had been dissolved. Table 5 in the Appendix shows the variation in the solubility of different gases, and also the fact that *gases are less soluble at higher temperatures*.

**85. Effect of Pressure on the Solubility of Gases.** In making soda water, carbon dioxide gas is forced into the soda fountain under a pressure of from 5 to 10 atmospheres. Many soft drinks, or carbonated waters, are made by forcing the carbon dioxide gas into the bottles under pressure. William Henry, an English chemist, learned that more gas can be dissolved in a liquid under an increase of pressure. HENRY'S LAW may be stated as follows: *The solubility of a gas in a liquid is directly proportional to the pressure at which the gas is supplied.* When soda water is drawn from a fountain, the pressure upon it is reduced to only one atmosphere. Much of the gas escapes with *effervescence*.

**86. Speed of Solution.** We may hasten the speed at which a solid dissolves in three ways: (1) *By stirring.* Agitating the mixture brings fresh portions of the solvent into contact with the solute. (2) *By powdering the solid.* Since solution can occur at the surface of the solute only, powdering the solute will make it dissolve more rapidly, because the amount of surface is increased tremendously. (3) *By heating.* An increase in temperature not only increases the total amount that can be dissolved, but it also increases the rate at which it dissolves.

**87. Freezing Point and Boiling Point of Solutions.** Those who live near the ocean know that *salt* water freezes at a lower temperature than *fresh* water. Sea water is a dilute, *unsaturated* solution. When it begins to freeze, the pure solvent (water) solidifies, and the solute it had contained forms with the unfrozen part of the solvent a more concentrated solution. This more concentrated solution has a still lower freezing point. It separates from the solute as it solidifies, leaving the remainder of the solution still more concentrated. This change continues until the solution that remains after successive freezings is saturated. A saturated solution of common salt, sodium chloride, has a *constant* freezing point,  $- 22^{\circ} \text{C}$ .

The student should keep in mind the fact that the word "salt" as used in chemistry applies to a group of compounds, often formed by the interaction of a base and an acid. For example, all the compounds except the first of those listed in Table 6 of the Appendix are salts. Common table salt is only one of a group of salts of which there are hundreds. It is characteristic, not of salts only, but of *solutes in general to lower the freezing point of the solvent.*

A salt added to water *raises* the boiling point of the water. This is also characteristic of solutes in general; *they raise the boiling point of the pure solvent.* When we boil a solution containing a solute that is *non-volatile*, the solvent disappears

by evaporation. Thus the solution becomes more and more concentrated as the boiling is continued, until it finally becomes saturated. In the meantime the boiling point of the solution gradually rises as the solution becomes more concentrated. This method of making a more concentrated solution by reducing its volume is known as *concentration by evaporation*.

When a solution of ammonia, which is a volatile solute, is boiled, the ammonia goes off into the air and the solute becomes more dilute. Such volatile solutes generally *lower* the boiling point, and the solution becomes more dilute as it is boiled.

## B. CRYSTALLIZATION

**88. Crystallization.** If we continue to concentrate a solution by evaporating the solvent, or if we cool a hot, saturated solution, some of the solute will separate from the solvent in the form of crystals. It is a characteristic habit of substances, when they are thrown out of solution as solids, or when they change from the liquid to the solid state by freezing, to form crystals having some regular, geometric pattern. For example, crystals of common salt are cubes; alum and diamond crystals are octahedral. The shape that the crystal takes is peculiar to the substance; hence it is sometimes possible to identify a substance by the shape of its crystals. (See Fig. 71.) We are all familiar with the fact that water forms crystals upon freezing; molten sulfur, sugar, or iron will form crystals in a similar manner upon solidifying or freezing.

Such substances as gelatine, glue, starch, and jelly do not form crystals. They belong to a class known as *colloids*, as contrasted with the *crystalloids*. The colloids do not form *true solutions*; they form what are called *colloidal suspensions*. Such suspensions are more fully discussed in Chapter 29.

**89. Why Crystallization Is Important.** The identification



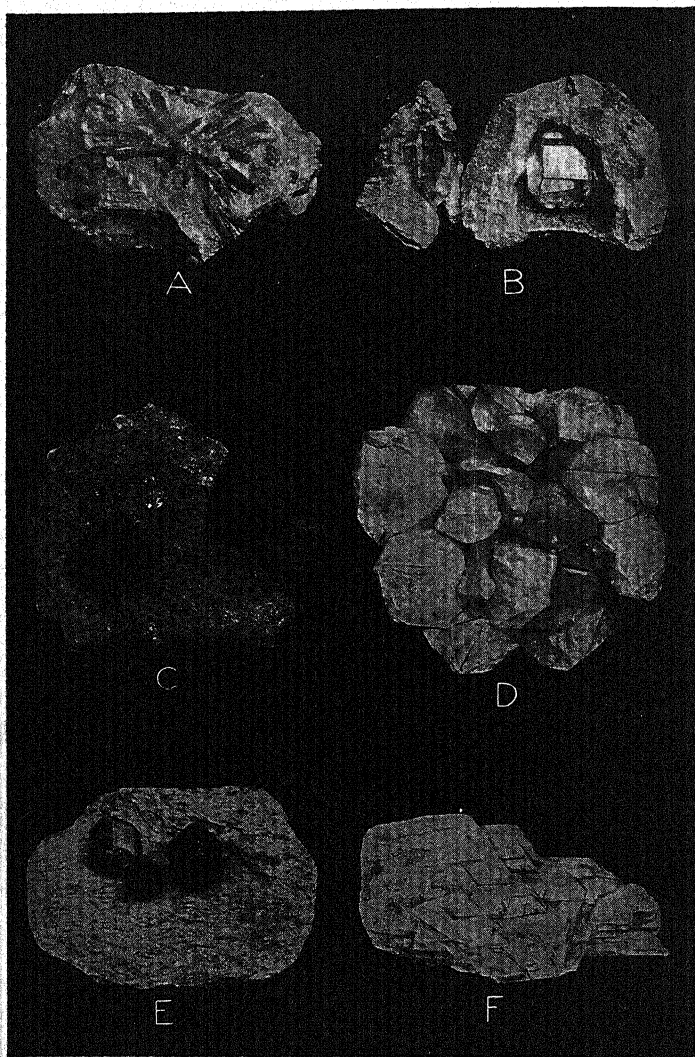


FIG. 71. — Plate of crystals. *a.* Rubellite. *b.* Quartz crystal in matrix. *c.* Galena. *d.* Quartz crystals. *e.* Garnets on rock. *f.* Gypsum.



of substances by the shape of their crystals may be considered one of the minor applications. Chemists purify substances by crystallization. Suppose we have some impure potassium nitrate which we wish to purify. We may dissolve the potassium nitrate in pure water and then evaporate part of the water. Crystals of potassium nitrate of quite a high degree of purity will separate from the solution. If we filter out these crystals and redissolve them in pure water, we may recrystallize them and get crystals of a higher degree of purity than before. Such recrystallization is much used in chemistry to obtain pure chemicals. The liquid that is left after a "crop" of crystals has formed is known as the "mother liquor." By evaporating it still farther, a second "crop" of crystals will be formed, but they will not be as pure as the first crystals.

If the solution is stirred while crystallization is taking place, finer crystals are formed. Small crystals thus rapidly produced are generally purer than large crystals formed more slowly, because the latter are more apt to have incorporated in them some of the mother liquor. If crystals that contain water thus mechanically held are heated they *decrepitate*. Steam is formed within the crystal and its expansion causes the crystal to burst open with a snapping sound.

Even when two different substances are present in a solution, they can sometimes be separated by *fractional crystallization*. When the solvent is evaporated, the less soluble substance will crystallize first, and it may be separated from the "mother liquor" by filtration.

If one looks over a stock of chemicals, he will find many different terms used to indicate the purity of the different chemicals. Some low-grade material is marked "commercial," or "technical." Purer chemicals may be marked "pure," "recrystallized," "U. S. P.," "highest purity," "crystallized from alcohol," and "C. P.," or "chemically pure." Unfortunately, *absolute* purity is impossible. Many

manufacturers of chemicals now send out "Analyzed Chemicals," in which the analysis is printed on the label. Then the chemist can tell just what impurity is present and in what quantity. (See Fig. 72.)

★ 90. **Supersaturated Solutions.** Let us add about 50 gm. of sodium thiosulfate, or what is commonly called "hypo" in photography, to 10 c.c. of water and try to dissolve all of

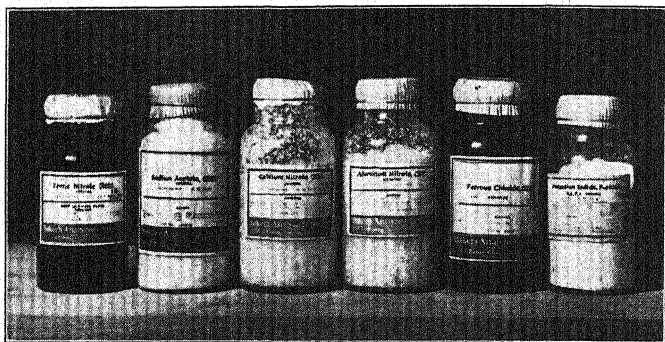


Photo by Wetlin

FIG. 72. — The analysis is sometimes printed on the label of the bottle.

it at room temperature, about  $20^{\circ}\text{C}$ . Not all of it will dissolve. If the temperature is raised to  $70^{\circ}\text{C}$ ., all of it will go into solution. We have just learned that usually crystals are formed when a saturated solution cools; but if we cool to room temperature the solution of "hypo" which we have just made, no crystals will be deposited. Such a solution is said to be *supersaturated*. It holds more solute than would be needed to saturate it at room temperature. Some substances readily form supersaturated solutions, but others show such tendency to only a slight degree.

We can show that a supersaturated solution is in a kind of unstable condition by dropping a small crystal of "hypo" into the supersaturated solution we prepared. This crystal

serves as a nucleus around which crystals of "hypo" immediately begin to form. Crystals continue to form, and heat is evolved, until we have left a solution, saturated at room temperature. Stirring a supersaturated solution, or scraping the inside of the containing vessel with a glass rod, will usually cause a supersaturated solution to crystallize.

**91. What Is Meant by Water of Crystallization?** In our study of water, we learned that it would combine with some crystals to form *hydrates*. We found that one molecule of copper sulfate would unite with five molecules of water to form a molecule of hydrated copper sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Water held in this manner by crystals is called *water of crystallization*. It is not to be confused with water held mechanically by a crystal, as discussed in Section 89. The fact that the crystals always hold a definite proportion of water is evidence that the water of crystallization is chemically combined with the salt itself.

A sodium carbonate molecule crystallizes with 10 molecules of water to form the crystallized salt,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . The water forms about 63% of the total weight of the crystal. The formula for crystallized sodium sulfate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , shows that ten molecules of water unite with one molecule of sodium sulfate as the latter crystallizes. Many other salts form hydrates, but there are a large number that never do. Sodium chloride, potassium chloride, and potassium chlorate do *not* contain water of crystallization.

If we heat a small crystal of copper sulfate in a test tube, the blue color and the glassy luster of the crystal will disappear as it slowly crumbles to a grayish white powder. The water that is driven off from the crystal collects on the cool walls of the tube. Such removal of water from a crystal is called *dehydration*, and the white powder that is left is *anhydrous* copper sulfate. This powder may be used as a *test for water*. When water is added to anhydrous copper sulfate, the color changes from white to blue.

**92. What Is Efflorescence?** Some crystals hold their water of crystallization so loosely that they lose a part or all of their water without being heated. A crystal that loses its water of crystallization when exposed to the air at ordinary temperature is said to be *efflorescent*. If we put on a scale pan a few freshly prepared crystals of sodium sulfate or sodium carbonate, and put enough shot on the other pan to counterpoise them, the crystals show a loss of weight after a few minutes' exposure. Water is given off and the crystals lose their luster, crumbling to a powder. *Efflorescence* occurs more readily in a very dry atmosphere than during damp rainy weather.

**93. What Is Deliquescence?** Let us place a few crystals of calcium chloride,  $\text{CaCl}_2$ , on a watch glass. Then we may counterpoise this glass on a balance as described in the preceding section. After a half hour, we shall find that the

crystals are gaining in weight. If we examine them carefully we find that they are also becoming moist, or even wet. Some crystals have the property of taking moisture from the air upon exposure, and even of dissolving in the moisture thus adsorbed. This property is called *deliquescence*. It is much more pronounced in damp, humid weather.

Some crystals, such as sodium chloride, or common table salt, attract moisture from the air and a slight film of moisture collects on their surfaces. They are said to be *hygroscopic*. Common table salt usually contains magnesium chloride,  $\text{MgCl}_2$ , as an impurity. This salt is deliquescent and becomes wet in damp weather, thus causing the table salt to "pack." Pure sodium chloride is not deliquescent.

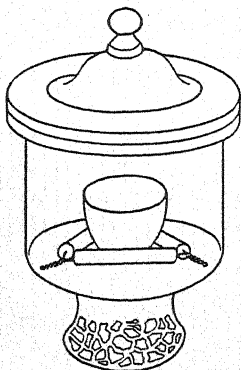


FIG. 73. — The material in the crucible is dried in the desiccator.

Deliquescent substances are used extensively for drying other substances. In the experiments on reduction and on determining the composition of water, the hydrogen was dried by passing it through a tube filled with calcium chloride, a deliquescent substance. The water formed in the latter experiment was adsorbed by the same compound. Figure 73 shows a desiccator used for drying compounds in the laboratory. The lower compartment is filled with deliquescent crystals.

### SUMMARY

A solution is a mixture consisting of a *solvent* and the *solute*. It has the following characteristics:

1. A solution is uniform throughout, or homogeneous.
2. The particles of a solution are so small that they cannot be removed by filtering.
3. The solute does not separate from the solvent upon standing.

The solubility of a substance is the ratio of the weight of solute to the weight of solvent, when the solution is saturated.

If the amount of solute is small compared to the amount of solvent, the solution is *dilute*. In a *concentrated* solution the weight of solute in the solvent is large.

In a *saturated* solution, the solvent holds all the solute it can at that particular temperature; the concentration is at its maximum.

Water is the most common solvent, although other liquids are often used. The solute may be a solid, a liquid, or a gas. Two liquids that are mutually soluble are said to be *miscible*.

In general, an increase in temperature increases the solubility of a solid. An increase in temperature decreases the solubility of a gas. The solubility of a gas is increased by an increase in pressure. This statement is known as Henry's Law.

The speed of a solution may be hastened: (1) *By stirring*; (2) *By raising the temperature*; (3) *By powdering the solute*.

Solids dissolved in a solvent raise the boiling point of the pure solvent and lower its freezing point. Gases dissolved in a solvent generally lower the boiling point of the solvent.

The cooling of a hot saturated solution, or the evaporation of a part of the solvent, will cause the separation of the solvent

in the form of crystals. The form of the crystal aids in its identification. Chemists use *recrystallization* as a method of purifying chemicals.

Water interacts with certain salts when they crystallize, thus forming *hydrates*. Hydrates lose their *water of crystallization* when they are heated. Hydrates that lose their water of crystallization on exposure to the air at ordinary temperature are said to be *efflorescent*.

Substances that take water from the air and become wet or dissolve in the water thus absorbed are said to be *deliquescent*. Deliquescent substances find use in drying moist substances. They are used in the laboratory in *desiccators*.

## QUESTIONS

### GROUP A

1. How would you proceed to make a saturated solution of common salt?
2. When emulsions are used as medicines, the bottle should be thoroughly shaken before using. Explain.
3. Why do soda fountains sometimes burst or explode?
4. Account for the rapid effervescence when a glass of "soda water" is drawn from the fountain. Why do bubbles of gas continue to arise from the liquid if it stands for a time?
5. Why do vegetables cook faster in a strong salt solution than they do in fresh water?
6. Why should bottles of calcium chloride be kept tightly stoppered?
7. Small open bottles containing calcium chloride are often placed inside the cases of clocks, electrical machines, and chemical balances. What is their use?
8. What is the meaning of the expression "concentrate by evaporation"?
9. How does leaving a bottle of "tincture of iodine" unstoppered affect its concentration? What bad results may come from such carelessness?
10. How does the addition of soap to dishwater aid in the cleansing process?

11. What physical principles are involved in the making of anti-freeze solutions for automobile radiators?

12. Explain why the first "crop" of crystals obtained during the crystallization of a solute is purer than those formed subsequently.

13. In what two ways may salt be obtained from the water of Great Salt Lake?

14. What principles are used in the processes of "dry" cleaning?

15. Calcium chloride is used in considerable quantities to sprinkle over dusty roads. Explain how it is useful in preventing clouds of dust.

#### GROUP B

16. If you were given a solution of sodium thiosulfate (hypo), how would you proceed to determine whether it was unsaturated, saturated, or supersaturated?

17. If you were given a solution containing both sodium chloride and potassium nitrate, how would you separate the two salts? Refer to the solubility curves, page 118, and explain whether the method you suggest would be suitable for use at a temperature of from 25° C. to 30° C.

18. Why do crystals of sugar often form in jellies or preserves that have stood a long time?

19. How does a solution differ from a chemical compound?

20. Would you prefer to buy crystals of washing soda (sodium carbonate) that had been kept in stoppered or in open boxes, if the price per pound were the same? Explain.

21. What two tests may show that a compound is water?

22. How is Henry's Law very much like the Law of Boyle?

23. If 100 gm. of water are saturated with potassium bromide at 100° C., and then cooled to room temperature, how many grams of potassium bromide will crystallize from the solution?

24. Explain why gas bubbles accumulate on the inside surface of a glass of ice water which stands in a warm room.

#### SUPPLEMENTARY PROJECT

Write a paper of about two hundred and fifty words on "The Importance of Solutions."



## CHAPTER 9

### PURIFICATION OF WATER — HARDNESS

#### Vocabulary

**Algae.** Sea-weeds, living in either fresh or salt water.

**Coagulum.** A bulky mass of precipitate.

**Distillation.** A process of purifying liquids by evaporating them and then condensing the vapor.

**Filtration.** The process of straining out solid matter held in suspension by a liquid.

**Pathogenic.** Causing disease.

**Zeolite.** A mineral that is capable of softening hard waters by exchanging its sodium for calcium.

**Sludge.** A slush or scum.

**94. Water Usually Contains Impurities.** Since water is such a good solvent, and no substance is absolutely insoluble, it is practically impossible to obtain pure water. The impurities present in water may be held: (1) in *suspension*; (2) in *solution*. Because of its buoyant effect water holds material in suspension. When water is in motion, upward currents are more or less prevalent. Thus it is possible for running water to carry more material in suspension. The amount of material water can carry depends upon the size of the particles and upon their density; it also increases as the velocity of the water is increased. When water stands quietly, all the matter it holds in suspension drops as sediment unless the matter has a density less than that of the water itself.

Rain water has very little matter in solution. It is *soft* water. Ground water contains considerable mineral matter in solution, since water is such a good general solvent. Water

that contains more than 50 parts of mineral matter dissolved in 1,000,000 parts of water is classed as *hard* water. Very hard water has over 100 parts per million. Some especially hard waters have 400 parts of mineral matter per 1,000,000.

**95. Kinds of Impurities.** Impurities in water are classed as: (1) *organic*; (2) *inorganic, or mineral*. Organic matter consists of bacteria, sewage, and other forms of animal and vegetable matter in various stages of decomposition or decay. As plants and animals decay, ammonia is formed. This ammonia is slowly oxidized first to nitrites and then to nitrates. The presence of more than a trace of ammonia, nitrites, or nitrates in drinking water indicates sewage contamination, or that the water is unwholesome. Much organic matter in water renders it unfit for drinking purposes, since such matter, though often harmless in itself, forms a breeding ground for all kinds of bacteria.

Either harmless or disease-producing bacteria may be present in drinking water. Epidemics of typhoid fever, dysentery, and cholera have often been traced to contaminated water supply. Typhoid fever has been nearly stamped out in cities where proper methods of purifying the water supply have been installed. During the Spanish-American War in 1898 typhoid fever caused the death of more soldiers than did the Spanish bullets. But better methods of securing sanitary drinking water were introduced before the World War began. Hence very few men died from typhoid fever. In the summer of 1898 the death rate from typhoid was 897 per 100,000 men. During the summer of 1918 it was only 3.3 per 100,000 men.

The nature of mineral matter in solution in water depends upon the composition of the soil and rock through which the water flows. Compounds of calcium, magnesium, sulfur, and iron are among the most common substances found in hard water. Since calcium compounds are found in the bones and teeth, their presence in water that is to be used for

drinking purposes is thought by some doctors to be desirable. Other doctors claim that mineral matter from hard water is not assimilated by the body at all.

**96. Methods of Purification.** Matter in *suspension* may be nearly all removed from water by three common mechanical processes: (1) by *sedimentation*; (2) by *sedimentation with coagulum*; (3) by *filtration*.

*Organic matter* is generally to a greater or lesser degree destroyed by the use of one or more of the following processes: (1) *aëration*; (2) *light*; (3) *ultra-violet rays*; (4) *boiling*; (5) *freezing*; (6) the *use of chemicals*.

Volatile matter is driven off when water is boiled, but non-volatile matter in *solution* can be removed only by *distillation*.

**97. Why Cities Have Water Problems.** In the country a farmer can get a supply of pure water by drilling a well deep enough to get water that has not been contaminated. Of course his well must be walled so that surface water cannot flow into it. If it is down in the valley, it must be protected against drainage from the stables or barns.

But as a city increases in size, the problem of securing an adequate supply of wholesome water becomes increasingly difficult and costly. Large areas must often be bought by the city, and the water in the lakes or streams within such area must be kept as free from organic refuse as possible. Of the methods of purifying water named above, filtration is most often used, either alone or in combination with other methods. If the water is roily it first goes to settling tanks or reservoirs.

**98. What Is Meant by Sedimentation?** Running water may carry considerable material in suspension either by rolling it along near the bottom of the stream or by carrying it nearer the surface by upward water currents. When such water is permitted to flow into settling basins or tanks, it soon loses nearly all the matter carried in suspension, since

gravity causes it to be deposited as *sediment*. Such sedimentation tanks or basins are used as a treatment of water preliminary to filtration.

**99. How Coagulum Aids Sedimentation.** When the particles of matter carried in suspension are very small, they settle slowly. Their deposition may be hastened by the use of some chemicals that will form a bulky precipitate, known as *coagulum*. As the precipitate settles, it then carries down

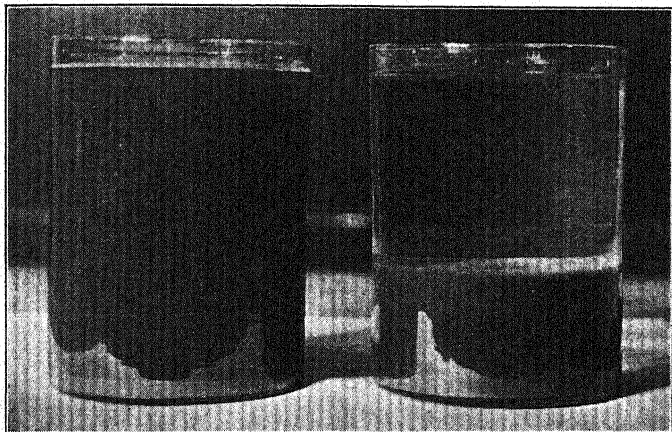
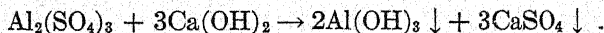


Photo by Wetlin

FIG. 74. — The jar at the left shows the turbid water to which the coagulum has been added. The water at the top of the jar at the right becomes clear as the mass settles.

with it the small particles held in suspension. If we add to some aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$ , a little slaked lime,  $\text{Ca}(\text{OH})_2$ , the two will interact and form aluminum hydroxide,  $\text{Al}(\text{OH})_3$ , and calcium sulfate,  $\text{CaSO}_4$ . The reaction is one of double substitution:



The aluminum hydroxide that is formed is a bulky, gelatinous precipitate, and the calcium sulfate is rather heavy.

Both sink to the bottom, carrying matter in suspension in the water along with them, and leaving the water very clear. (See Fig. 74.) A considerable per cent of the bacteria present in the water is enmeshed and carried down with such a coagulum. Ferrous sulfate is sometimes used instead of the sulfate of aluminum. In waters that are moderately hard, the mineral matter in the water itself interacts with the

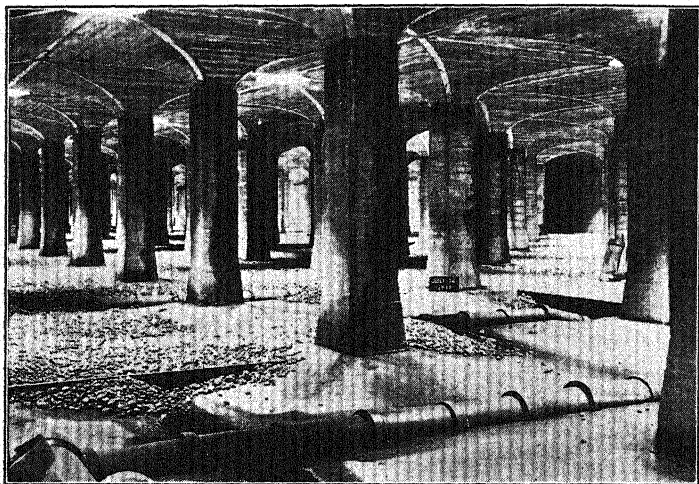


FIG. 75. — Filtration beds showing connection with water mains.

aluminum sulfate and makes the addition of the slaked lime unnecessary.

**100. Filtration Is an Important Method of Purifying Water.** If water is permitted to trickle through sand, the impurities that are held in suspension are strained out. This is a natural method of purifying some spring waters. The bacteria and the organic matter are destroyed by oxidation. The efficiency of *natural sand filtration* depends upon the nature of the soil, and upon the distance the water travels through uncontaminated soil. A sandy or gravelly soil is best. If a well is in a valley, and nearby houses and stables

are situated on higher ground, the soil through which the water percolates may become contaminated with pathogenic bacteria. Filtration through such a soil becomes a menace.

*Slow sand filters.* City water is often filtered through layers of sand and gravel acres in extent and several feet thick. Layers of charcoal may be used between the sand and gravel to remove coloring matter and gases having dis-

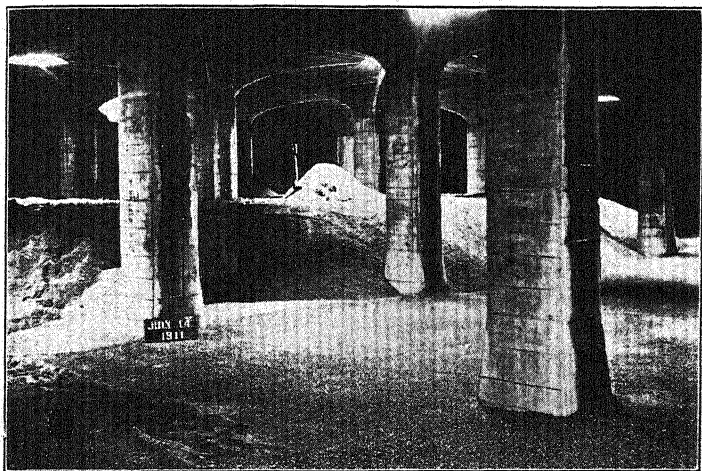


FIG. 76. — A portion of the same filtration beds filled with sand ready for filtration.

agreeable odors. At the bottom the filtered water collects in tile drains which transmit it to the city mains. (See Fig. 75.) A gelatinous layer soon collects on the top, thus aiding the purification, partially because of more perfect filtration and partially because microorganisms that destroy bacteria collect in this layer. As the rate of filtration becomes more and more retarded, it is necessary to scrape off this surface layer occasionally. These filtration plants are expensive to install, since they should be covered to prevent freezing. (See Fig. 76.) Then, too, certain green water plants known as *al-*



*gae* grow in reservoirs in the presence of sunlight. They are sometimes called "pond-scum." Some algae secrete an oil that gives to the water a fishy or pig-pen odor and a disagreeable taste.

*Mechanical Filters.* Mechanical filters are rapid sand filters that are generally used with coagulation systems. The water is run into large tanks and treated with the

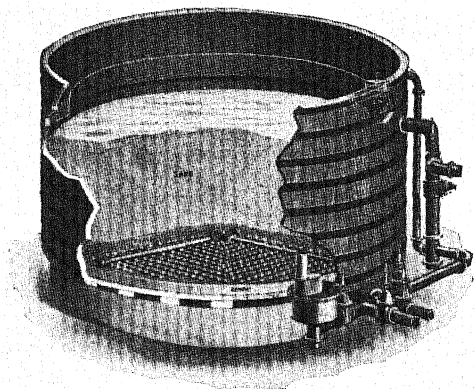


FIG. 77. — Gravity type of mechanical filter.

chemicals as in the coagulum method described above. The partially clarified water is then strained rapidly through the sand and gravel layers in the mechanical filter. Figure 77 shows a mechanical filter of the gravity type.

In Fig. 78 a pressure filter is shown. When mechanical filters need to be cleaned, water is forced through them in the reverse direction, the impurities being carried into the sewer with the wash water. The revolving rakes shown in the figure aid the cleansing process by breaking up the bed of filtering material.

**101. Household Filters.** Many persons have the idea that a bag of charcoal tied over the faucet or pump-spout will filter out all impurities. Such a filter is worse than use-



less since it soon becomes clogged and forms a breeding place for bacteria. In the *Pasteur filter*, however, the water is forced under pressure through a cylinder of unglazed porcelain.

The bacteria and other impurities collect on the outside of the porcelain, which should be cleaned frequently and sterilized by heating to about  $110^{\circ}\text{C}$ . The Berkefeld filter (Fig. 79)

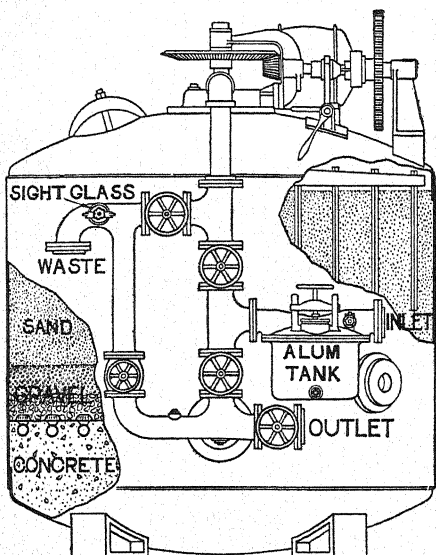


FIG. 78. — Mechanical filter of the pressure type.

is similar in construction. The same company makes an *army type filter* with which water from a stream may be filtered by the use of a small portable pump.

### 102. The Importance of Aëration.

Only surface water comes into contact with the oxygen of the air. When the water is agitated fresh portions are brought to the surface. In some reservoirs fountains have been installed which cause the water to spout up into the air and flow back over a large

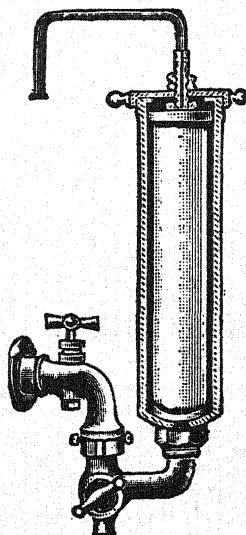


FIG. 79. — Porcelain filter.

surface in thin layers. In some cases compressed air bubbles up through the water in the reservoir. In still other cases aëration is accomplished by letting the water flow over a

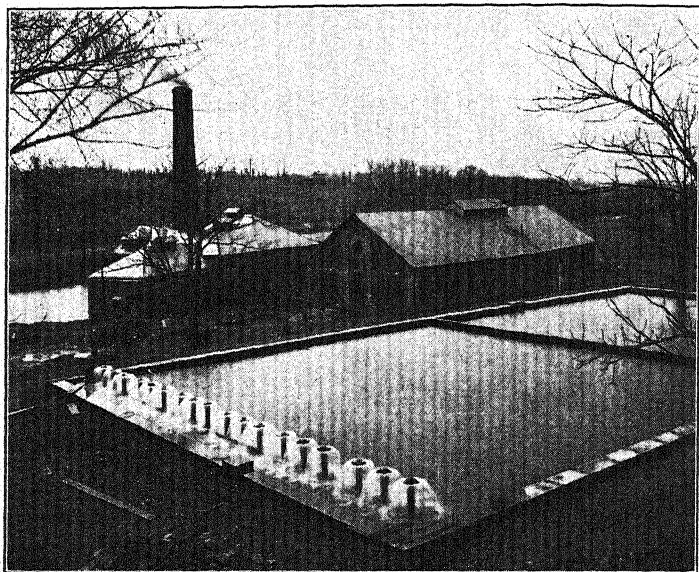


FIG. 80. — Purification of water by aëration.

series of cascades as it enters the reservoir. Aëration oxidizes organic matter and some of the bacteria are destroyed. Gases having disagreeable odors are also removed by this method of purification. (See Fig. 80.)

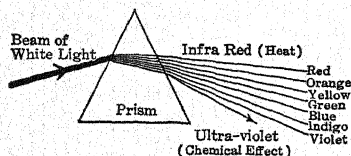


FIG. 81. — A prism separates white light into its seven colors.

**103. Light Helps to Destroy Bacteria.** Sunlight is useful in destroying bacteria. It is not very valuable for water purification, however, since it does not

penetrate the water to a very great depth. Thus only the

surface layers are affected. Furthermore, light promotes the growth of algae. We have already learned that it is desirable to have filtration beds covered, since algae need light for their growth. To keep open reservoirs free from algae costs cities a considerable sum each year.

**104. Ultra-violet Rays Destroy Bacteria.** If the sun's rays are passed through a prism and allowed to fall upon a screen, we can see a band of colors. (See Fig. 81.) A thermometer placed just beyond the red shows that heat rays are present, although we cannot see them. A photographic plate placed just beyond the violet is darkened by rays which are invisible, but very active chemically.

These rays are known as *ultra-violet* light. They are very active in destroying bacteria. They can be prepared artificially by the use of incandescent mercury vapor inclosed in a *quartz* tube. They do not pass through ordinary glass readily, but special glass is now being made that transmits ultra-violet rays fairly well. Figure 82 shows a phantom view of an ultra-violet sterilizer. Victor Henri showed that water exposed to ultra-violet light as it flows quite rapidly through the apparatus is rendered practically free from

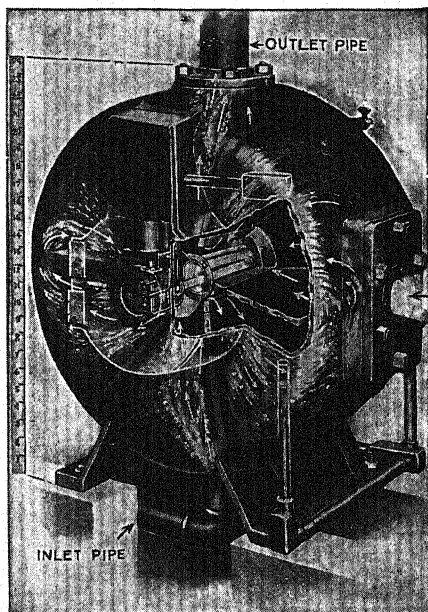
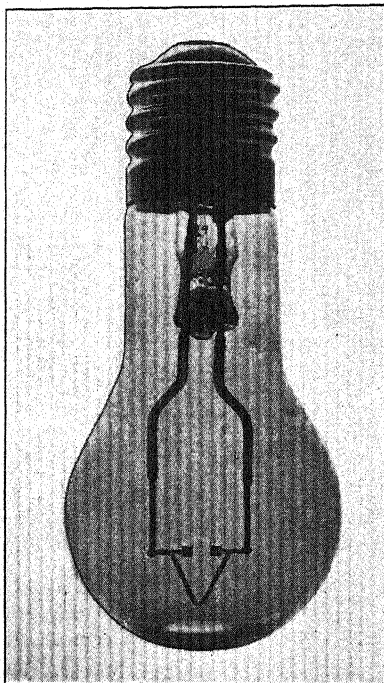


FIG. 82. — Phantom view of a water sterilizer.

bacteria. Unfortunately quartz tubes have been very expensive. It is to be hoped that the new glass will prove satisfactory, so that ultra-violet rays may be used not only to sterilize water for drinking purposes and swimming

pools, but that our electric bulbs that supply us with visible light may also supply us with the ultra-violet rays that are beneficial to health when properly used. The mercury vapor arc in a quartz tube supplies abundant ultra-violet rays that will kill bacteria, burn the flesh, cause colors to fade rapidly, and produce many other chemical effects. Such lamps are too dangerous to be used except under the direction of a physician. Figure 83 shows a new socket lamp that may be used to produce ultra-violet rays. Special glass is used in making the bulb.



*Courtesy of General Electric Co.*

FIG. 83. — The small tungsten filament becomes hot and the globule of mercury at the bottom of the bulb is vaporized. The arc of mercury vapor emits ultra-violet rays.

temperature of  $100^{\circ}$  C. for more than a few minutes. Disease-producing bacteria are generally destroyed if the boiling temperature is maintained for from 15 to 30 minutes.

**105. Boiling Destroys Bacteria.** Very few bacteria can withstand a

Of course boiling is impractical for large-scale purification. It should be practiced, however, when the water supply is low in dry weather, and when one must drink water of doubtful purity. After water is boiled it has a flat taste. It becomes more palatable if it is thoroughly aerated after the boiling.

**106. Freezing Destroys Some Bacteria.** Many bacteria are destroyed at the temperature at which water freezes. Therefore ice is purer than the water from which it was obtained. Ice for use in foods should always be made from

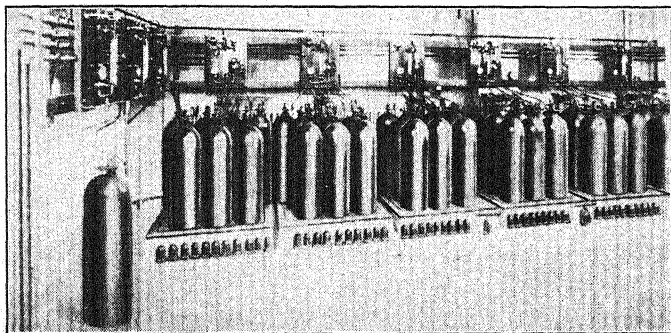


FIG. 84. — Rows of liquid chlorine cylinders.

pure water, because some bacteria can resist the freezing temperature.

**107. Chemicals Used to Purify Water.** Several different chemicals are used in water purification. Generally they are used in connection with one or more of the other methods. The use of chemicals affords the cheapest and surest method of destroying bacteria. The following find use:

1. **Ozone.** Under the study of ozone, its use in water purification was mentioned. Since it leaves nothing in the water but oxygen, it is satisfactory and efficient. It is difficult to make ozonizers that give a satisfactory yield of

ozone. This fact alone prevents a more extensive use of this gas for water purification.

2. *Chlorine*. Probably no chemical is so widely used to purify water for drinking purposes and in swimming pools as chlorine. This gas is easily liquefied and it is inexpensive, since it is made from common table salt, sodium chloride ( $\text{NaCl}$ ). (See Fig. 84.) The chlorine gas may be released from such cylinders directly into the water.

3. *Silver*. The Congressional Country Club has installed a device for sterilizing a 150,000-gallon swimming pool with metallic silver. Less than one ounce of finely divided silver will destroy the bacteria in 1000 tons of water.

4. *Copper sulfate*. No chemical seems to be so effective in keeping city reservoirs free from algae as copper sulfate.

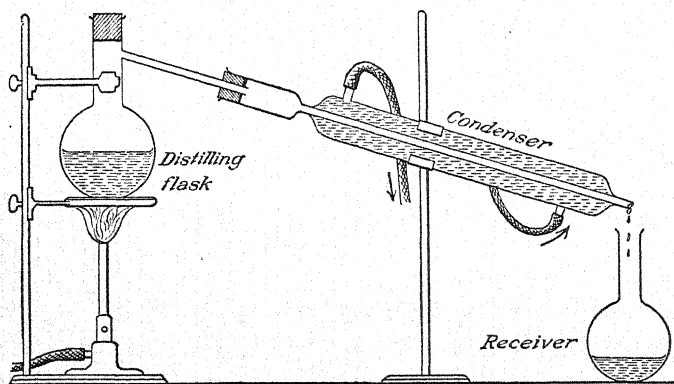


FIG. 85. — Laboratory apparatus for purifying liquids by distillation.

It is also very active as a germicide. It is claimed that so small a quantity as 1 part in 10,000,000 parts of water will destroy the bacteria that cause typhoid fever. Used in small quantities, it is very satisfactory as a purifier.

**108. How Water Is Freed from Impurities in Solution.**  
In all the methods we have discussed for purifying water,



we have considered only impurities held in suspension. From the standpoint of health, they are most important, since they aim to remove bacteria or to destroy them. If water contains mineral matter dissolved in it that makes the water poisonous or injurious to health, another source of supply must be found. Distillation is the only method in use for obtaining water free from matter in solution. This process, however, is too expensive to be used on a large scale. Distilled water finds its chief uses in making ice, for filling storage batteries, and in certain chemical industries.

1. *Distillation.* In the laboratory we may distil water by using a flask with a side neck as shown in Fig. 85. The water to be distilled is placed in the flask and boiled to convert it into vapor. The condenser consists of two concentric tubes, through the outer of which cold water flows continuously. The vapor from the distilling flask passes through the inner tube and it is there cooled and condensed to a liquid by the cold water flowing around it. The distilled water is collected in the receiver.

Water may be obtained in a reasonably pure state by distillation. Since any gases or volatile matter will readily be driven off by the heat, the first portion of the distillate should be rejected. The non-volatile matter remains in the distilling flask. Figure 86 shows one type of continuous action still. The water that is used for condensation later flows into the still. Thus it is somewhat preheated by the heat of condensation.

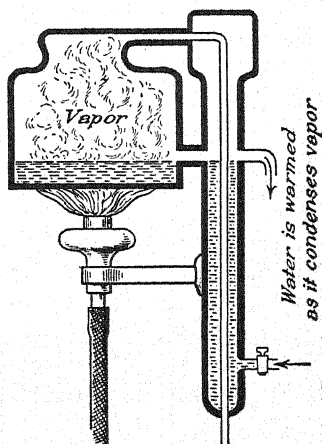


FIG. 86. — A continuous action water still.

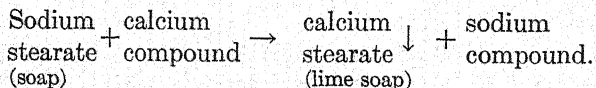


The student should not get the idea that distillation is used only for the purification of water. It is extensively used in purifying other liquids. In fact practically any liquid that does not decompose at the temperature of its boiling point may be purified in this manner. We define *distillation* as a process consisting of evaporation and subsequent condensation.

2. *Fractional distillation.* Liquids that have different boiling points may usually be separated by *fractional distillation*. To illustrate, petroleum is composed of several substances boiling at different temperatures. The petroleum is heated at a low temperature until the oils having a very low boiling point, such as naphtha, petroleum ether, gasoline, and benzine, are all volatilized and condensed. The temperature is raised until gas oil distillates are vaporized. At a still higher temperature various grades of lubricating oil and paraffin oil are obtained.

#### HARDNESS OF WATER \*

109. **What Makes Waters Hard?** We have already learned that mineral matter dissolved in water produces what is called hard water. The mineral matter which is most objectionable is that which forms a precipitate with soap, or "curdles" soap. The most common mineral matter found in hard waters consists of compounds of calcium, magnesium, or iron. Soap is a substance that consists largely of such compounds as sodium stearate. It is easily soluble in soft water. If we add some soap to a water that contains some compound of calcium, for example, a double decomposition reaction occurs as represented by the word equation:

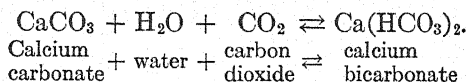


The calcium stearate, or "lime soap," is insoluble in water, and forms a precipitate that sticks to the sides of the

\* Hard waters may be studied under calcium, Chap. 32.

bath tub or wash basin when soap is used with hard water for our ablutions. Magnesium and iron compounds present in hard waters behave in a similar manner and form objectionable precipitates by combining with soap. Furthermore, no soapsuds can be formed in hard water until enough soap has been added to precipitate all the calcium and magnesium compounds that are present. Thus large quantities of soap are wasted.

110. "Temporary" and "Permanent" Hard Waters. When water that has carbon dioxide dissolved in it flows over limestone ( $\text{CaCO}_3$ ), it dissolves some of the limestone and forms *calcium bicarbonate*.



The calcium *bicarbonate* is about 90 times as soluble as calcium *carbonate*. Hence, water in limestone regions is likely to be very hard. If the water containing such bicarbonates is boiled, then the reaction is reversed, and calcium carbonate is precipitated. The bicarbonates of magnesium and iron behave in a similar manner. Hard waters that contain bicarbonates of such compounds are called "*temporary hard waters*" because they may be softened by boiling. Students who live in limestone regions are familiar with the crust of calcium carbonate that forms on the bottom of the tea-kettle from the decomposition of the calcium bicarbonate during boiling.

The name "*permanent hard water*" is given to those waters that contain mineral matter which is not precipitated by boiling. The name is misleading, since they can be softened by the use of chemicals. The "permanent hard waters" usually contain such minerals as the sulfates of calcium and magnesium. Magnesium sulfate is *readily* soluble in water, but calcium sulfate is only *slightly* soluble.

111. *Objections to the Use of Hard Waters.* 1. *For laundry purposes.* If suds cannot be formed until all the mineral matter in the water has combined with the soap and been precipitated, evidently much soap will be wasted if hard water is used for laundry purposes. Then, too, the precipitate accumulates in the pores of the fabric, giving the garment a dingy appearance after washing. It is difficult to rinse such a precipitate out of the garment, since it adheres to the fibers with considerable persistence.

2. *For steam boilers.* It takes several tons of water to run a passenger train from New York to Buffalo. That water is evaporated to produce steam for power purposes. If the water contained mineral matter, it would remain after the evaporation and form an incrustation known as "boiler scale." (See Fig. 87.) Such a scale is a very poor conductor of heat and more fuel is needed to produce steam if even a thin scale is present. Engineers estimate that a magnesium scale  $\frac{3}{64}$  in. thick will cause a loss of 25% in the fuel value. The iron walls of boiler flues that become partially clogged with scale may be heated to a red heat



FIG. 87.—Pipe nearly closed by scale.

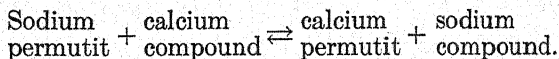
and they sometimes burst under the pressure of the steam.

Hard waters also produce corrosion or "pitting" in steam boilers, thus decreasing the life of the boiler or its flues. Dissolved oxygen and carbon dioxide are probably active in aiding such corrosion.

3. *In other industries.* Mineral matter present in the water used in the dyeing industry may cause uneven dyeing, or the color itself may be altered. Hard water may cause stains upon the leather in leather manufactures, or upon paper in the paper industry. In soap factories, sugar refineries, and in chemical manufacturing plants, hard water is objection-

able. Automobile radiators soon lose in efficiency if the water used in them is very hard, and the water used for replenishing storage batteries must be free from mineral matter.

**112. How Hard Waters Are Softened.** The chemistry of softening hard waters will be more fully discussed in a later chapter. Some common methods are mentioned briefly: (1) Waters which have "temporary hardness" are softened by boiling, or by adding *slaked lime* to precipitate the bicarbonates which cause the hardness. The precipitate is then allowed to settle. (2) *Washing soda* ( $\text{Na}_2\text{CO}_3$ ) is one of the cheapest and most efficient of the commercial water softeners. *Borax* is used on a small scale but it is too expensive for extensive commercial use. (3) *Tri-sodium phosphate* is coming into use. (4) Such substances as graphite, tannin, glue, etc., are added to water so the scale formed in boilers will be softer and more easily removed. They do not remove the hardness, but find use as "boiler compounds" because they mix with the scale and make it soft enough to be removed by scraping or to be blown off as a sludge by the use of steam pressure. (5) *Zeolite softeners* are now extensively used. Some natural minerals, sodium silico-aluminates, will exchange their sodium for the calcium or magnesium in a hard water as the water flows over them, or stands in contact with them. Several different companies are now manufacturing such minerals in granular form for softening water by filtration. They are used under such names as "duro," "decalso," and "permutit." Figure 88 shows a tank packed with granular permutit for use in softening water by filtering the water through it. The word equation for the reaction follows:



Thus the calcium is removed from the water, and we have a water of zero hardness. The reaction is reversible, and the

calcium may be removed from the permutit again by the use of a concentrated solution of common salt, sodium chloride. Then the permutit takes sodium from the salt, and it is *regenerated* so that it may be used over and over again.

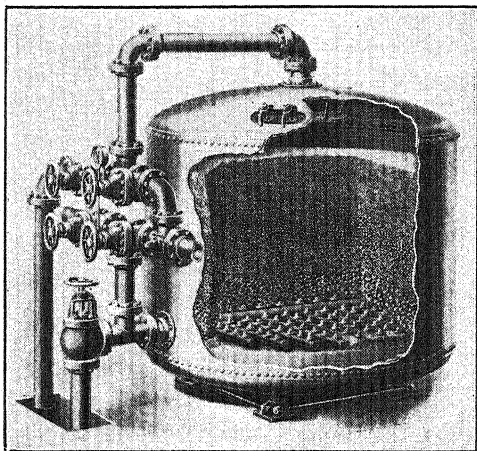


FIG. 88. — Water softener, using artificial zeolite.

Softeners of these types are manufactured for softening water for dwelling houses, for swimming pools, and for power plants. Several cities are now installing municipal softening plants. (See Fig. 89.)

### SUMMARY

Impurities present in water may be held: (1) in *suspension*; (2) in *solution*. The impurities held in suspension are: (1) *organic*; (2) *inorganic*.

Impurities held in suspension may be removed from water in several ways: (1) *sedimentation*; (2) *sedimentation with the use of coagulum*; (3) *filtration*. In the latter case, use is made of *natural soil filtration*, *filtration beds*, and *mechanical filters*.

Organic matter including bacteria may be destroyed in several

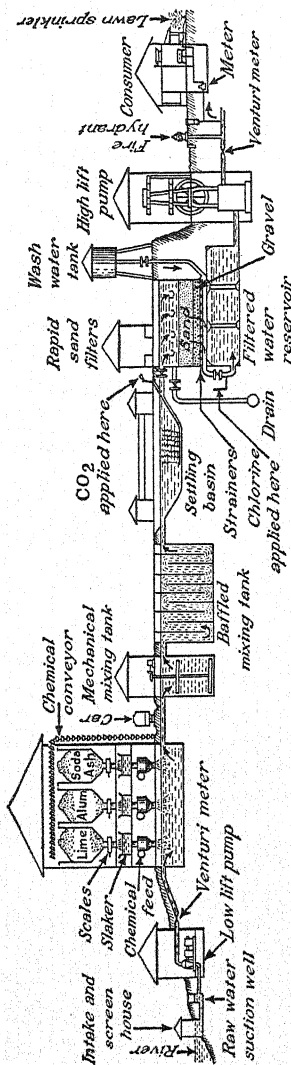


FIG. 89. — Diagrammatic scheme to show how water is purified and softened at Columbus, Ohio. From the Scioto River the water flows through screens into a suction well, whence it is pumped through a venturi meter to the purifiers. Here the chemicals needed to purify and soften the water are added. For 10 min. it is then mixed. After being agitated in the baffled mixing tank, the water then flows to the settling basins. Enough carbon dioxide is added to neutralize any excess lime and to convert the carbonates into bicarbonates. After carbonation the water goes to the filters, where it is filtered through 24 in. of sand and 18 in. of gravel. As the water comes from the filters it is treated with a small amount of chlorine, the average amount being 0.15 parts per million.

ways: (1) *aëration*; (2) *sunlight*; (3) *ultra-violet rays*; (4) *boiling*; (5) *freezing*; (6) the use of *chemicals*, such as *ozone*, *chlorine*, *silver*, and *copper sulfate*.

Mineral matter dissolved in water may be removed by *distillation*. This process of evaporating liquids and condensing their vapors is used in purifying liquids. Liquids having different boiling points may be separated from each other by *fractional distillation*.

Hard water contains in solution mineral matter that will curdle soap. Very hard water may contain several hundred parts of mineral matter per million parts of water. If the mineral matter is precipitated by boiling, it is said to have *temporary hardness*. Water having mineral matter that cannot be removed by boiling is said to have *permanent hardness*. Such hard water can be softened, however, by the use of chemicals.

Hard waters waste soap, corrode boilers, produce boiler scale, and interfere in the manufacture of many industrial products.

On a small scale borax may be used to soften hard waters. *Slaked lime* and *washing soda* (sodium carbonate) are extensively used in the industries for softening hard waters. *Artificial zeolites* are also used for this purpose.

## QUESTIONS

### GROUP A

1. Distinguish between "pure water" and "wholesome water."
2. Should you use filtered water or distilled water for making up solutions in a chemical laboratory? Give reasons for your answer.
3. Why is it necessary to keep water at the boiling temperature for some minutes to sterilize it?
4. Explain how you would proceed to determine whether a sample of water contains mineral matter in solution.
5. What is the purest form of natural water? Explain.
6. Is rain water satisfactory for use in storage batteries? Give a reason for your answer.
7. Bread is organic matter. Is it objectionable in the water of a city reservoir? Explain.



8. If water tends to purify itself upon freezing, is the ice obtained from the waters of a polluted stream suitable for use in iced tea? Give a reason for your answer.

## GROUP B

9. Why should drinking water that shows the presence of ammonia, nitrites, or nitrates be looked upon with suspicion?

10. Why is a good microscope needed in a sanitary water analysis?

11. If you were given a sample of water containing both volatile and non-volatile matter, how should you proceed to get pure water from it?

12. Why are small household filters attached to water faucets likely to become a menace rather than a protection?

13. How would you proceed to determine the amount of mineral matter present in a sample of sea water?

14. How could you treat sea water so the last part of Coleridge's rhyme "Water, water everywhere, and not a drop to drink" would be untrue?

15. Why is the name 'permanent hard water' not a good one?

16. Write a three-hundred-word essay upon the subject: 'Are hard waters undesirable for drinking purposes?'

## SUPPLEMENTARY PROJECT

Investigate, and prepare a report on, the methods used for purifying the water of your city.

Suggested reference: See report published by the Water Department in your city, or consult the engineer in charge.

## CHAPTER 10

### ATOMIC THEORY — ATOMIC WEIGHTS

#### Vocabulary

**Combining weight.** The weight of an element needed to combine with 1 gram of hydrogen.

**Reacting weight.** The weight of an element needed to combine with or to displace 1 gram of hydrogen.

**Theory.** An explanation of scientific phenomena, supported by considerable evidence, but not capable of laboratory demonstration.

**113. Atoms Have a Definite Combining Weight.** In the analysis of water we found that 1 part by weight of hydrogen combines with approximately 8 parts by weight of oxygen to form 9 parts by weight of water. In a similar manner, it is possible to analyze hydrogen chloride,  $\text{HCl}$ . The analysis shows that it is composed of 1 part by weight of hydrogen to 35.5 parts by weight of chlorine. Similar analyses of ammonia,  $\text{NH}_3$ , marsh gas,  $\text{CH}_4$ , and hydrogen sulfide,  $\text{H}_2\text{S}$ , show that:

1 gram of hydrogen combines with 4.66 gm. of nitrogen.

1 gram of hydrogen combines with 3.0 gm. of carbon.

1 gram of hydrogen combines with 16.0 gm. of sulfur.

It is possible to multiply such examples, but in every case we find that hydrogen has a smaller *combining weight* than any other element. Hence we use *hydrogen as the standard for combining weight relations*. *The combining weight of an element is the weight of that element which combines with one gram of hydrogen.*

It is of interest to inquire how these elements combine with

one another. In certain compounds familiar to chemists, analyses show that:

- 8 gm. of oxygen combine with 4.66 gm. of nitrogen.
- 8 gm. of oxygen combine with 3.00 gm. of carbon.
- 3 gm. of carbon combine with 16.00 gm. of sulfur.
- 3 gm. of carbon combine with 35.50 gm. of chlorine.

A comparison of these figures shows us that these elements combine with each other in the same proportion that they combine with hydrogen. We call 8 the combining weight of oxygen, not only because it combines with one gram of hydrogen, but also because 8 gm. of oxygen will combine with 4.66 gm. of nitrogen, or 3 gm. of carbon.

Now we are in a position to understand more fully just what Lavoisier did for chemistry when he introduced the use of the balance. (See Fig. 34.) The manufacturer who wishes to make a chemical compound weighs out the different *factors* in the ratios of their *combining weights*. For example, the combining weight of iron is 28, and the combining weight of sulfur is 16. If we wish to make 44 lb. of iron sulfide,  $\text{FeS}$ , we weigh out 28 lb. of iron, and heat it with 16 lb. of sulfur. Of course we can get iron sulfide by heating 40 lb. of iron with 16 lb. of sulfur, but in that case 12 lb. of iron would be left uncombined, an extravagant waste.

Our grandmothers used to make their own baking powder by mixing 2 parts of cream of tartar with 1 part of baking soda. But a chemical analysis shows that 188 parts by weight of cream of tartar react with 84 parts by weight of baking soda.  $188 \div 84 = 2.23$ . The correct proportion is 2.23 parts to 1 part, instead of 2 to 1. That means that our grandmothers used nearly two ounces too much baking soda in making three pounds of baking powder. That is a small item for one household, but enough to make the cakes or biscuits bitter, and sufficient waste of one chemical to ruin the business of a large manufacturer. Their use of a spoon for measuring also gave inaccurate results.

**114. Reacting Weights.** Some elements do not combine with hydrogen at all, and we cannot find their combining weights directly. In a *substitution* reaction, such elements will *displace* hydrogen from its compounds. It is interesting to find that the weight of an element needed to replace 1 gm. of hydrogen from its compound is exactly the same as the weight of that element that combines with 8 gm. of oxygen, the combining weight of oxygen. For example,

23 gm. of sodium combine with	8 gm. of oxygen.
23 gm. of sodium displace	1 gm. of hydrogen.
12 gm. of magnesium combine with	8 gm. of oxygen.
12 gm. of magnesium displace	1 gm. of hydrogen.

Thus we observe that the combining weight, and the weight of an element that will *substitute* itself for 1 gram of hydrogen, are numerically the same. For this reason, the term *reacting weight* is often used to apply to both combining weight and displacement weight.

Of course the Law of Definite Proportions could not be true if elements did not have a definite combining or reacting weight. This law is based upon chemical analysis.

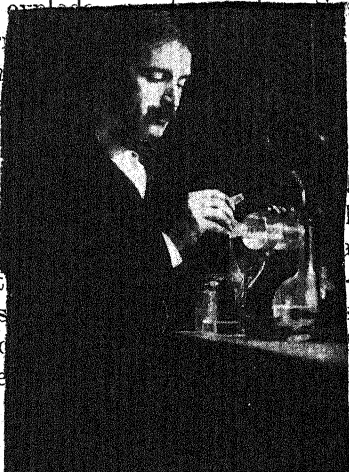
We find by analysis that 1 part by weight of hydrogen combines with 8 parts by weight of oxygen in the compound water. In hydrogen peroxide, however, 1 part of hydrogen combines with 16 parts by weight of oxygen. Thus we see that *oxygen may have more than one combining weight*. The higher combining weight is always a *multiple* of the lower. The fact that some elements have more than one combining weight is just what we would expect from the fact that in some cases two elements unite to form a *series of compounds*. The Law of Multiple Proportions is merely a statement of these facts.

**115. What Is the Atomic Theory?** We have already learned that the chemist can subdivide matter into atoms, but that he cannot subdivide the *atom*. The early scientists believed that matter could be subdivided to infinity, but a

different conception of matter was proposed by John Dalton in his *atomic theory*. We shall find that some modifications are necessary, due to the light of modern research, but his views form a good working basis for the chemist. Dalton's ideas were about as follows:

1. *Matter is made up of very small particles called atoms.*
2. *Such atoms are indivisible by chemical means.* (We know that some of them are made up of still smaller particles. See Chap. 40 for new ideas concerning atoms.)
3. *The atom of an element has a certain weight.*
4. *The atoms of different elements have different weights.*
5. *Chemical affinity is the attraction between atoms of different elements.*

A mason may arrange bricks in houses of different design. He may also build a house more by using bricks of different sizes. In a similar manner, the chemist arranges them to form thousands of different compounds at his disposal 92 different kinds of atoms of different weights. The mason has one brick, but the chemist can cut a brick into two parts. The atoms, however, cannot divide an atom by any



Courtesy of Mrs. Richards.

**116. What Is Meant by Atomic Weight?**  
 Atoms are too small to be weighed directly. The chemist must know the *actual weight* of the atoms. This is of the greatest importance for him. His work in redetermining atomic weights was characterized by its extreme accuracy. He weighs one-millionth or one-billionth of a milligram, but it is of vital interest to know *how many times as heavy the sulfur atom is as the oxygen atom*. Because oxygen occurs in so many compounds, chemists have agreed to use the weight of the *oxygen atom as a standard*, and to determine the weights of the atoms of all other elements by comparing them with the weight of the oxygen atom. If we refer to the

table of atomic weights as printed on the inside of the back cover of this book, we see that the *weight of oxygen is assumed to be 16*. The sulfur atom is a little more than twice as heavy as the oxygen atom. Hence the atomic weight of sulfur is 32.06. The weight of the bromine atom is almost five times that of the oxygen atom; its atomic weight is 79.92. The student is not expected to memorize atomic weights. In

23 gm. of sodium combine w  
23 gm. of sodium displace  
12 gm. of magnesium combin  
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use in solving problems in beginning chemistry, the table of  
*approximate* weights as given on the inside of the front cover  
may be used.

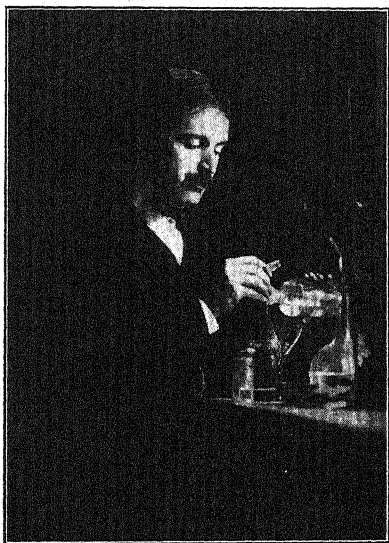
fact, the figures are fre-  
quently revised as more re-  
fined methods of analysis  
make it possible to determine  
atomic weights with greater  
accuracy. Jons Jakob  
Berzelius was one of the first  
chemists to make accurate  
atomic weight determina-  
tions. (See Fig. 90.) Others  
who spent much time in such  
determinations were Jean  
Dumas and Jean Stas. Pro-  
fessor Theodore W. Richards,  
of Harvard University, was  
awarded the Nobel Prize in  
chemistry in 1914 for his  
elaborate analytical methods  
that led to the most accurate  
atomic weight determinations  
yet made. (See Fig. 91.) For

**117. How Dalton's Atomic Theory Harmonizes with Dalton's Laws.** If the weight of the carbon atom is 12, and the weight of the oxygen atom is 16, then we would expect 12 parts by weight of carbon to combine with 16 parts by

weight of oxygen to form 28 parts by weight of carbon monoxide, because one molecule of carbon monoxide ( $\text{CO}$ ) contains one atom of carbon and one atom of oxygen. The weight of the carbon atom is definite (12) and different from the weight of the oxygen atom, which is also definite (16). Since these atoms are *indivisible* by chemical means, they must always unite in a *definite proportion by weight*.

In the compound carbon dioxide,  $\text{CO}_2$ , we have one atom of carbon, atomic weight equals 12, and two atoms of oxygen, atomic weight of each equals 16, combined to make one molecule. This, too, accords with the *law of definite proportions*. But the weight of the carbon is the same for both compounds; in the latter,  $\text{CO}_2$ , we have added one more atom of oxygen. Of course the weight of oxygen is just doubled; it is a multiple of the weight of the oxygen in carbon monoxide. The law of *multiple proportions* must be true if atoms have a definite weight and are indivisible. Adding another atom increases the weight by a fixed amount.

**118. The Significance of Chemical Formulas.** We are now able to understand a fuller significance of chemical



Courtesy of Mrs. Richards

FIG. 91. — Theodore W. Richards (1868–1928) was a distinguished American chemist. He is well known through the methods of accurate analysis that he devised. His work in redetermining atomic weights was characterized by its extreme accuracy.



formulas. The formula,  $\text{H}_2\text{O}$ , represents: (a) 1 molecule of water; (b) it shows that each molecule of water contains 2 atoms of hydrogen and 1 atom of oxygen; (c) it represents 2 parts by weight of hydrogen (each atom of hydrogen having a weight of 1) and 16 parts by weight of oxygen; (d) it stands for 18 parts by weight of water.

In any chemical formula the small number that follows any symbol shows the number of such atoms in the molecule. For example,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , the formula for cane sugar, shows that each molecule of sugar contains 12 atoms of carbon, 22 atoms of hydrogen, and 11 atoms of oxygen. It also signifies 144 ( $12 \times 12$ ) parts by weight of carbon, 22 ( $22 \times 1$ ) parts by weight of hydrogen, 176 ( $11 \times 16$ ) parts by weight of oxygen, and 342 parts by weight of sugar.

A number that precedes a formula shows the number of molecules used. For example,  $5\text{H}_2\text{SO}_4$  stands for 5 molecules of sulfuric acid, each molecule containing 2 hydrogen atoms, 1 sulfur atom, and 4 oxygen atoms. The formula for copper nitrate,  $\text{Cu}(\text{NO}_3)_2$ , shows that each molecule contains 1 atom of copper, 2 atoms of nitrogen, and 6 atoms of oxygen. The formula is written  $\text{Cu}(\text{NO}_3)_2$  instead of  $\text{CuN}_2\text{O}_6$ , because the group of elements ( $\text{NO}_3$ ) behaves like a single element.

### 119. How to Find Molecular Weights from Formulas.

If the formula for water ( $\text{H}_2\text{O}$ ) represents one molecule of water, and shows that it is composed of two atoms of hydrogen, each having a weight of 1, and one atom of oxygen, having a weight of 16, then *we can find the molecular weight by adding together the weights of all the atoms in the molecule*. In the compound aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$ , we have in one molecule:

2 Al atoms (wt. 27 each)	total, 54 parts by weight.
3 S atoms (wt. 32 each)	total, 96 parts by weight.
12 O atoms (wt. 16 each)	total, 192 parts by weight.
Molecular weight equals grand total, <u>342</u> .	

**120. How to Find the Per Cent of Any Element in a Compound.** If we have a table of atomic weights and know the formula of a compound, we can find by simple arithmetic the per cent of any element. We must first find the molecular weight as in the preceding section by adding together the sums of the weights of *all* the atoms in the compound, as shown by the formula. Then, just as we find what per cent \$80 is of \$200 by *dividing the part by the whole*, so we divide *the sum of the weights of all the atoms of that element whose per cent is to be found by the molecular weight of the compound*.

Suppose we wish to find what per cent of potassium chlorate,  $\text{KClO}_3$ , is oxygen.

SOLUTION: K, 1 atom	weight, 39.0
Cl, 1 atom	weight, 35.5
O <sub>3</sub> , 3 atoms	weight, <u>48.0</u> ( $3 \times 16$ )
molecular weight, 122.5	

Then, 48 (parts by weight of oxygen)  $\div$  122.5 (molecular weight) equals 0.3918, equivalent to 39.18% of oxygen. In a similar manner we find by dividing the atomic weight of potassium (39) by the molecular weight that this compound contains 31.83% of potassium. By dividing 35.5, the atomic weight of chlorine, by the molecular weight, we find the per cent of chlorine in potassium chlorate to be 28.98.

Often the compound contains water of crystallization. Sodium carbonate may be taken as an example of such a compound. Its formula is  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . The formula shows that 10 molecules of water have crystallized with 1 molecule of sodium carbonate to form the hydrate. The period indicates water of crystallization; it is not a sign of multiplication here.

$2 \times 23$ , or	46 parts by weight are sodium, Na
$1 \times 12$ , or	12 parts by weight are carbon, C
$3 \times 16$ , or	48 parts by weight are oxygen, O
$10\text{H}_2\text{O} = 10 \times 18$ , or	<u>180</u> parts by weight are water, $\text{H}_2\text{O}$
286 parts by weight are crystallized sodium carbonate.	

$46 \div 286 = 0.1608$ , equivalent to 16.08% of sodium.

$12 \div 286 = 0.042$ , equivalent to 4.20% of carbon.

$48 \div 286 = 0.1678$ , equivalent to 16.78% of oxygen.

$180 \div 286 = 0.6293$ , equivalent to 62.93% of water, eight-ninths of which is oxygen; one-ninth, hydrogen.

### 121. How to Find the Simplest Formula of a Compound.

The student has probably wondered how the chemist finds the relative number of atoms in a formula. He may be interested to know why the formula for water is  $\text{H}_2\text{O}$ , and the formula for nitric acid is  $\text{HNO}_3$ . Before such a formula can be found, the compound must be analyzed to find its percentage composition. Then by use of the table of atomic weights, one can find the *relative* number of particles or atoms in the molecule of the compound. The simplest formula may then be written by using the symbols with the relative numbers of each atom.

Given the following data: A compound is found by analysis to be 75% carbon and 25% hydrogen. Out of every 100 parts by weight in this compound, 75 parts are made up of carbon atoms that have a relative weight of 12; and 25 parts by weight are made up of hydrogen atoms that have an approximate weight of one. If we divide 75, the per cent of carbon, by the atomic weight of carbon, 12, we have a quotient of 6.25. If we divide 25, the per cent of hydrogen, by its atomic weight, 1, we get a quotient of 25. *The ratios of these two quotients give us the relative number of carbon and hydrogen atoms in the compound.* We have 6.25 atoms of carbon for every 25 atoms of hydrogen. We cannot write the formula  $\text{C}_{6.25}\text{H}_{25}$ , because we cannot have *fractions* of atoms. If we divide both numbers by 6.25, we find that there is 1 carbon atom for every 4 hydrogen atoms. The formula becomes  $\text{CH}_4$ , which is the *simplest* formula of this compound.

**PROBLEM.** A compound contains carbon, 40%; hydrogen, 6.66%; and oxygen, 53.33%. Find its simplest formula. Let us tabulate our results as follows:

Element	Symbol	Per Cent	Atomic Weight	Per Cent divided by Atomic Weight
Carbon.....	C	40.00	12	3.33
Hydrogen.....	H	6.66	1	6.66
Oxygen.....	O	53.33	16	3.33

To find the simplest ratio, we divide the quotients by the smallest quotient.

$$\begin{array}{r} 3.33 \overline{) 3.33 - 6.66 - 3.33} \\ 1 \quad - \quad 2 \quad - \quad 1 \end{array}$$

The simplest formula of the compound is  $\text{CH}_2\text{O}$ .

PROBLEM. A compound contains carbon, 81.81%; hydrogen, 18.18%. Find its simplest formula.

Element	Symbol	Per Cent	Atomic Weight	Per Cent divided by Atomic Weight
Carbon.....	C	81.81	12	6.82
Hydrogen.....	H	18.18	1	18.18

$$\begin{array}{r} 6.82 \overline{) 6.82 - 18.18} \\ 1 \quad - \quad 2.66 \end{array}$$

Since there can be no fractional atoms, we find the simplest *whole number* ratio by clearing of fractions. Thus  $\frac{3}{2}$  and  $2\frac{3}{2}$  have the ratio of 3 to 8. The formula is  $\text{C}_3\text{H}_8$ .

To find the simplest formula of a compound: (1) *Divide the per cent of each element by its atomic weight*; (2) *Find the whole number ratio of these quotients*; (3) *Write the symbols of each element, using enough atoms to correspond with the ratio found*.

## SUMMARY

The *combining weight* of an element may be defined as the weight of that element that will combine with one gram of hydrogen. Some elements have more than one combining weight.

The term *reacting weight* is often used to apply to the weight of

an element that will combine with one gram of hydrogen, or displace one gram of hydrogen by substitution.

The *atomic theory* may be summarized as follows:

1. Matter is made up of atoms which are indivisible by chemical means.
2. The atom of an element has a definite weight.
3. The atoms of different elements have different weights.
4. Chemical affinity is the attraction between atoms.

The *atomic weight* of an element is that number which tells the weight of its atoms as compared to the weight of the oxygen atom, which is 16. The atomic weight of an element either equals the combining weight, or it is a multiple of the combining weight.

The fact that atoms have a definite weight, and that atoms are indivisible, explains why the laws of definite and multiple proportions must be true.

Chemical formulas show the composition of a compound, qualitatively and quantitatively. From the formula, one can find the percentage composition of a compound.

One may find the simplest formula of a compound by: (1) analyzing the compound to find the per cent of each element in it; (2) dividing the per cent of each element by the atomic weight of that element; (3) finding the simplest whole number ratio of the quotients obtained in (2); (4) writing the symbols in order, following each one by the corresponding quotient obtained in (3).

### QUESTIONS

1. How does a theory differ from a law?
2. State fully the meaning of each of the following formulas:  $\text{HNO}_3$ ;  $\text{KCl}$ ;  $\text{Ca}(\text{OH})_2$ ;  $4\text{ZnCl}_2$ ;  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ;  $\text{Ca}_3(\text{PO}_4)_2$ .
3. What is the difference between  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4$ ? What changes would you expect the former compound to undergo, if it were heated to  $100^\circ \text{C}.$ ?
4. In finding the molecular weight of a compound from its formula, what precautions must be taken?
5. Outline the separate steps needed for the finding of the simplest formula of a compound.

## PROBLEMS

## GROUP A

(Use approximate atomic weights as given on front cover.)

1. Find the percentage composition of each of the following:  $\text{Fe}_2\text{O}_3$ ;  $\text{HgO}$ ;  $\text{NaCl}$ .
2. What per cent of sodium sulfate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , is water?
3. Find the per cent of nitrogen in each of the following:  $\text{Ca}(\text{NO}_3)_2$ ;  $\text{CaCN}_2$ ;  $(\text{NH}_4)_2\text{SO}_4$ .
4. Which would yield more chlorine per ton, sodium chloride,  $\text{NaCl}$ , or potassium chloride,  $\text{KCl}$ ?
5. Find the simplest formula of a compound containing carbon, 92.31%; hydrogen, 7.69%.
6. Analysis of a compound shows that it contains: Potassium, 39%; hydrogen, 1%; carbon, 12%; and oxygen, 48%. Find its simplest formula.
7. Find the simplest formula of a compound having the following composition: Sodium, 28.05%; carbon, 29.26%; hydrogen, 3.66%; and oxygen, 39.02%.
8. Find the simplest formula. Analysis: Carbon, 64.86%; hydrogen, 13.52%; and oxygen, 21.62%.
9. Analysis: Nitrogen, 21.21%; hydrogen, 6.06%; sulfur, 24.24%; oxygen, 48.48%. Find the simplest formula.
10. Analysis: Calcium, 19.32%; chlorine, 34.30%; oxygen, 46.38%. Find the simplest formula.

## GROUP B

11. Find the simplest formula for a compound having the following analysis: Phosphorus, 43.66%; oxygen, 56.33%.
12. A compound has the following composition: Iron, 70%; oxygen, 30%. Find its simplest formula.
13. Analysis: Hydrogen, 3.06%; phosphorus, 31.63%; oxygen, 65.30%. Find its simplest formula.
14. A compound is made up of the following elements: Sodium, 37.70%; silicon, 22.95%; oxygen, 39.34%. Find its simplest formula.
15. A compound is made up of the following: Carbon, 52.17%;

hydrogen, 13.04%; and oxygen, 34.78%. Find its simplest formula.

16. Analysis: Calcium, 31.25%; carbon, 18.75%; oxygen, 50.00%. Find the simplest formula.

17. Analysis: Carbon, 8.57%; hydrogen, 0.71%; and iodine, 90.71%. Find the simplest formula.

18. Analysis: Calcium, 24.69%; hydrogen, 1.23%; carbon, 14.81%; and oxygen, 59.26%. Find the simplest formula.

19. A compound contains: Sodium, 47.91%; aluminum, 18.75%; and oxygen, 33.33%. Find its simplest formula.

20. Find the simplest formula of a compound that has the following analysis: Potassium, 24.68%; manganese, 34.81%; and oxygen, 40.50%.



If we use a large circle to represent one molecule, and small circles within it to represent atoms, we may picture the relationship between molecules and volumes, as in Fig. 94.

It is interesting to note that in the first equation, one volume of hydrogen and one volume of chlorine form two volumes of hydrogen chloride. In the second equation,

2 vols. hydrogen + 1 vol. oxygen  $\rightarrow$  *only* 2 vols. vapor.

There is a contraction in this case because each of the new molecules that are formed contains *three* atoms instead of *two*. We started with three molecules of two atoms each, and had formed two molecules of three atoms each. In dealing with equations where all the substances are gaseous, the *relative number of volumes is always the same as the number of molecules*. In the third case illustrated, we find that 3 volumes of hydrogen and 1 volume of nitrogen form *only two* volumes of ammonia. The ammonia molecule,  $\text{NH}_3$ , contains *four* atoms. *No atoms are lost during a chemical change, and there is no change in weight*, but the volumes vary because the atoms may combine to form *fewer* molecules.

In a similar manner it may be shown that *the molecules of all ordinary gaseous elements contain two atoms*. The molecules of some elements that are liquid or solid at the ordinary temperature do not contain two atoms when they are vaporized. For example, mercury and iodine have at high temperatures *only one atom* to the molecule. Phosphorus has four; sulfur, 2, 4, or 8, varying with the temperature.

★ 125. **What is Meant by a Mole?** We have learned how to find the molecular weight from the formula. If we weigh out as many grams of a substance as are exactly equal to its molecular weight, we have what chemists call the *gram-molecular weight* of a substance, or *one mole*. For example, one mole of hydrogen chloride,  $\text{HCl}$ , is the molecular weight ( $1 + 35.5$ ), multiplied by 1 gram. To find one mole of sulfuric acid, we first find its molecular weight. ( $2 + 32$

+ 64 = 98.) Then, one mole equals 98, the molecular weight,  $\times 1$  gm., or 98 gm. One mole of oxygen,  $O_2$ , is equal to 32 gm., since we have just proved that one molecule of oxygen contains two atoms.

★ 126. What Is a Molar Solution? If we weigh out exactly *one mole* of a substance and then dissolve it in enough water to make 1000 c.c. of solution, we have a *molar solution*. Much time may be saved by making up considerable quantities of such solutions in the laboratory. When a chemist measures out 100 c.c. of a molar solution, he knows how many grams of the solute are present without the necessity of a separate weighing.

★ 127. How Much Space Does One Mole of a Gas Occupy? We have learned that it is very difficult to weigh gases accurately. But we may find the space occupied by one mole of certain gases of which we know the weight. For example, we know that one liter of hydrogen at S. T. P. weighs 0.09 gm., and that one mole of hydrogen,  $H_2$ , equals 2.016 gm. ( $2 \times 1.008 \times 1$  gm.) Now we may calculate the number of liters of hydrogen that will be needed to weigh 2.016 gm. If we divide 2.016 by 0.09, we find that *it will take 22.4 liters of hydrogen to make one mole*. We know that one liter of oxygen at S. T. P. weighs 1.43 gm., and that one mole of oxygen equals 32 gm. But,  $32 \div 1.43 = 22.4$ , the number of liters in one mole of oxygen.

We could go on and make calculations with other gases, but it is unnecessary. Avogadro's law tells us that equal volumes of all gases at the same temperature and pressure have the same number of molecules. *Therefore, a mole of one gas will occupy the same space as one mole of any other gas*. Experiments also show that this is true. The student should remember that *one mole of any gas at standard temperature and pressure occupies 22.4 liters of space*. This volume, 22.4 liters, is sometimes called the *gram-molecular volume*, since it is the volume occupied by one *gram-molecular weight*.

★ 128. How to Find the Weight of One Liter of Any Gas. Suppose we wish to find the weight of one liter of sulfur dioxide,  $\text{SO}_2$ , at S. T. P. We may use the knowledge gained in the preceding section to calculate such weight. For example, 22.4 liters of sulfur dioxide weigh as many grams as one mole, which equals 64 gm. ( $32 + (2 \times 16)$ ). Then,  $64 \text{ gm.} \div 22.4 = 2.85 \text{ gm.}$ , the weight of one liter of sulfur dioxide at S. T. P. *We may find the weight of one liter of any gas at S. T. P. by dividing the molecular weight of that gas in grams by 22.4 liters.*

$$D \text{ (gm. per liter at S. T. P.)} = \frac{\text{gm. mol. wt.}}{22.4}$$

From the molecular weight of a gas, one can tell at a glance whether the gas is heavier or lighter than air. One liter of air weighs 1.29 gm. 22.4 liters of air will weigh  $22.4 \times 1.29 \text{ gm.}$ , or 28.95 gm. Suppose we wish to know whether acetylene gas is heavier or lighter than air. Its formula is  $\text{C}_2\text{H}_2$ . Its molecular weight is 26. By comparing this number with 28.95, we find that acetylene is lighter than air. The molecular weight of the gas hydrogen sulfide,  $\text{H}_2\text{S}$ , is 34. It is heavier than air. By dividing 34 by 28.95, we find that it is 1.17 times as heavy. Its specific weight, air standard, is 1.17.

★ 129. How to Determine the Molecular Weight. 1. *Of a gas, or of a substance that can be vaporized without decomposing.* Since we know that one mole of any gas at S. T. P. occupies 22.4 liters, we can use that knowledge to find the molecular weight of a gas, even if we do not know its formula. We find the weight in grams of 22.4 liters of that gas at S. T. P. This may be done by weighing 1 liter of the gas in grams, and then calculating the weight of 22,400 c.c., or 22.4 liters, at S. T. P. Or, we may construct a box that holds 22.4 liters, find its weight in grams, and fill it at standard conditions with the vapor of the substance whose molecular weight is to be found. (See Fig. 95.) *The increase in weight in grams is equal to the molecular weight of the substance.*

Suppose we weigh one liter of a gas at standard conditions and find that it weighs 1.25 gm. Then 22.4 liters of that gas will weigh  $22.4 \times 1.25$  gm., or 28 gm. Therefore, the molecular weight of the gas is 28.

It is not practicable to weigh a gas at S. T. P. Of course any temperature and pressure can be used, because it is possible by the use of the laws of Charles and Boyle to compute the weight at standard conditions.

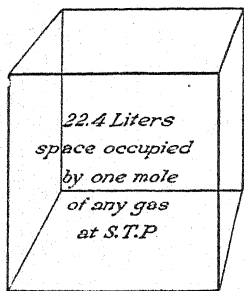


FIG. 95. — A 22.4-liter box.

2. Of a compound that cannot be vaporized. If we try to evaporate such a compound as sugar, we find that it decomposes. Hence we cannot find its molecular weight by getting the weight in grams of 22.4 liters of its vapor. In such cases we make use of the fact that a *solute lowers the freezing point of a solvent*. François

Raoult, a French chemist, found that if he dissolved one mole of alcohol, 46 gm., in 1000 gm. of water that the water would not freeze at  $0^{\circ}\text{C}$ ., but that the solute would lower the freezing point of the solvent  $1.87^{\circ}\text{C}$ . Many other substances behave in a similar manner. A molal solution of glucose freezes at  $-1.87^{\circ}\text{C}$ . Further experiments show that one mole of any substance, *except an acid, a base, or a salt*, lowers the freezing point  $1.87^{\circ}\text{C}$ . when dissolved in one liter of water. Hence, to find the molecular weight of a non-volatile, but *soluble*, substance, we merely find the number of grams that must be dissolved in 1000 gm. of water to lower its freezing point  $1.87^{\circ}\text{C}$ .

Raoult also found that one mole of a non-volatile substance, with the *exception of acids, bases, and salts*, dissolved in 1000 gm. of water will raise the boiling point of the solvent  $0.52^{\circ}\text{C}$ . Hence we may also find the molecular weight of a non-volatile substance by determining the number of grams that

must be dissolved in 1000 grams of water to raise the boiling point  $0.52^{\circ}\text{C}$ . In general, the freezing point and boiling point methods of finding molecular weights give only approximate results.

3. *Non-volatile, insoluble substances.* No one has yet succeeded in working out a method for finding the molecular weight of a substance that can neither be vaporized nor dissolved in some solvent. The percentage composition and the simplest formula of such substances can be found, but not the molecular weight. Starch is such a substance. Its simplest formula is  $\text{C}_6\text{H}_{10}\text{O}_5$ . But its formula could be  $\text{C}_{12}\text{H}_{20}\text{O}_{10}$ , or some other multiple of the simplest formula. Chemists write its formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ , but the value of  $x$  is unknown.

★ 130. **How to Find the Correct Formula of a Compound.** Students frequently ask why the formula for hydrogen peroxide is written  $\text{H}_2\text{O}_2$ , instead of  $\text{HO}$ ,  $\text{H}_3\text{O}_3$ , or some similar formula. The percentage composition as found from the formulas  $\text{HO}$ ,  $\text{H}_2\text{O}_2$ , or  $\text{H}_3\text{O}_3$  is the same in all cases. From the percentage composition, we find that the *simplest* formula is  $\text{HO}$ . But to find out the *correct* formula, we must determine the molecular weight to see whether it is 17, 34, 51, or some other number. If the molecular weight is 17, then the correct formula is  $\text{HO}$ . But we find that the molecular weight is 34; therefore  $\text{H}_2\text{O}_2$  is the *correct formula*. Each atom of the simplest formula  $\text{HO}$  must be taken twice to give a molecular weight of 34, which experiment shows to be correct.

**PROBLEM.** A compound contains carbon, 92.31%; hydrogen, 7.69%. One liter of its vapor at S. T. P. weighs 3.482 gm. Find its *correct* formula.

**SOLUTION.** By the method given in Section 121 we first find its simplest formula, which is  $\text{CH}$ . If 1 liter weighs 3.482 gm., then 22.4 liters will weigh  $3.482 \times 22.4$ , or 78 gm. The molecular weight of the compound is 78. But the molecular weight of the

simplest formula is only 13, as we find by adding the atomic weights. Let  $x$  equal the number of times each element must be taken. Then  $13x = 78$ , and  $x = 6$ . It is obvious that each atom of the simplest formula must be taken 6 times to give the molecular weight, 78. The correct formula is  $C_6H_6$ .

### SUMMARY

According to the Law of Gay-Lussac the combining volumes of all gases may be expressed by small whole numbers. If the product is gaseous, it bears a simple whole number ratio to the factors.

From Avogadro's Law we learn that equal volumes of all gases have the same number of molecules, provided they have the same temperature and pressure.

From these laws pertaining to gases, it is possible to show that *one molecule of a gaseous element contains two atoms*. Therefore, the letter H represents a single atom of hydrogen; 2H represents two atoms of hydrogen; but  $H_2$  represents one molecule of hydrogen that contains two atoms.

One *mole* of any substance is equal to its molecular weight times 1 gram. It is also called the *gram-molecular weight*. A *molar solution* contains one mole of the solute in one liter of the solution.

One mole of any gas at S. T. P. occupies 22.4 liters. We can find the weight of one liter of any gas by dividing its molecular weight in grams by 22.4. The weight of 22.4 liters of air is 28.95 gm. If the molecular weight of a gas is more than 28.95, that gas is heavier than air, and conversely.

To find the molecular weight of a gas or of a volatile compound, we find the weight in grams of 22.4 liters of its vapor at standard temperature and pressure. The weight in grams is numerically equal to its molecular weight.

To find the molecular weight of a soluble, non-volatile compound, we determine the number of grams that must be dissolved in 1000 gm. of water to lower its freezing point  $1.87^\circ C.$ , or to raise its boiling point  $0.52^\circ C.$  That number equals the molecular weight. This method does not apply to acids, bases, and salts. The reason for this exception is given in Chap. 21.

## QUESTIONS

## GROUP B

1. How would you prove that the nitrogen molecule contains two atoms?
2. Formulate a rule for finding the correct formula of a compound.
3. Suppose you are given a compound whose percentage composition is given, but whose molecular weight is unknown. How would you proceed to find its correct formula?
4. What relation is there between the coefficients of gases in an equation and their relative volumes?
5. Why do we not speak of 28.95 as the molecular weight of the air?

## PROBLEMS

## GROUP B

1. Five hundred c.c. of a gas at S. T. P. weigh 0.98 gm. Calculate the molecular weight of the gas.
2. One liter of a certain gas collected at a pressure of 720 mm. and at a temperature of  $27^{\circ}\text{C}$ . weighs 1.30 gm. Calculate its molecular weight.
3. One liter of chlorine at S. T. P. weighs 3.17 gm. Find the molecular weight of chlorine. From this molecular weight, what do you infer as to the number of atoms in a molecule of chlorine?
4. At standard conditions 225 c.c. of sulfur dioxide weigh 0.6428 gm. Find the molecular weight of sulfur dioxide.
5. The compounds  $\text{HBr}$ ,  $\text{PH}_3$ , and  $\text{N}_2\text{O}$  are all gaseous at the ordinary temperature. Find their molecular weights. From an inspection of their molecular weights, tell which ones are heavier than air. Calculate their specific weight, air standard.
6. Calculate the weight of one liter of hydrogen chloride,  $\text{HCl}$ , at S. T. P. Find how many times as heavy this gas is as air.
7. Find the weight of one liter of the following gases:  $\text{CH}_4$ ;  $\text{NH}_3$ ;  $\text{C}_2\text{H}_2$ .
8. Calculate the weight of one liter of nitrogen. Find its specific weight, air standard.
9. Calculate the weight of 400 c.c. of the following gases:



$\text{CO}_2$ ;  $\text{H}_2\text{S}$ . Can you calculate the weight of 400 c.c. of common salt,  $\text{NaCl}$ , by the same method? Explain.

10. Find the weight of one liter of water vapor. Compare this weight with the weight of one liter of air. Compare this weight with the weight of one liter of liquid water. How many volumes of water vapor would be formed by the evaporation of one liter of water at  $100^\circ \text{C}$ ?

11. A compound contains nitrogen, 30.51%; oxygen, 69.49%. Two hundred c.c. of the gas at S. T. P. weigh 0.817 gm. Find the simplest formula, the molecular weight, and the correct formula for this compound.

12. By analysis a compound is found to contain hydrogen, 5%; fluorine, 95%. Four hundred c.c. of the gas weigh 0.714 gm. Find the simplest formula, the molecular weight, and the correct formula for this compound.

13. One liter of alcohol vapor weighs 1.592 gm. at a temperature of  $78^\circ \text{C}$ . and under a pressure of 760 mm. of mercury. Find the molecular weight of alcohol. Hint: One liter of alcohol calculated at  $0^\circ \text{C}$ . weighs more than 1 liter at  $78^\circ \text{C}$ .

14. A compound shows the following analysis: Carbon, 32%; hydrogen, 4%; oxygen, 64%. Find its simplest formula. Fifteen gm. of this substance added to 1000 gm. of water lower its freezing point  $0.187^\circ \text{C}$ . Find the molecular weight and the correct formula.

15. A compound contains 80% of carbon; the rest is hydrogen. Find its simplest formula. Two hundred c.c. of its vapor at S. T. P. weigh 0.268 gm. Find its molecular weight, and its correct formula.

16. A compound shows the following analysis: Carbon, 26.67%; hydrogen, 2.22%; and oxygen, 71.11%. Find its simplest formula. The molecular weight of the substance is 90. Find its correct formula.

17. Analysis: Carbon, 40%; hydrogen, 6.67%; and oxygen, 53.33%. Find its simplest formula. Eighteen gm. of this compound dissolved in 1000 gm. of water raise the boiling point of the water  $0.052^\circ \text{C}$ . Calculate the molecular weight of the compound and its correct formula.

18. A compound has the formula  $\text{C}_2\text{H}_4\text{O}_2$ . The compound is volatile. From this formula, make a problem similar to number 11.

## CHAPTER 12

# WHAT IS VALENCE — HOW VALENCE IS USED

### Vocabulary

**Valence.** The capacity which one atom of an element has for holding in combination hydrogen atoms.

**Radical.** A group of elements that generally behaves chemically as if it were a single element.

**Ternary.** A compound that contains three elements.

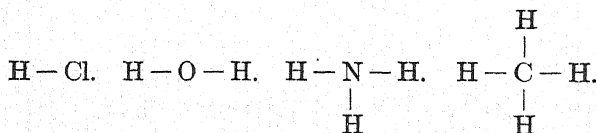
**Proton.** A positively charged particle equal in weight to the hydrogen atom.

**131. Introductory.** The student has probably wondered why we write the formula for hydrogen chloride,  $\text{HCl}$ ; for water,  $\text{H}_2\text{O}$ ; for ammonia,  $\text{NH}_3$ ; and for methane or marsh gas,  $\text{CH}_4$ . We observe that one atom of chlorine can hold *only* one atom of hydrogen in combination. We say it has a valence of one. An oxygen atom is capable of holding in combination *two* atoms of hydrogen; its valence is two. The nitrogen atom, which can hold *three* hydrogen atoms, is said to have a valence of three. The carbon atom may have a valence of four, since it can hold in combination *four* hydrogen atoms. The carbon atom has a greater capacity for holding hydrogen atoms than has either the nitrogen or the oxygen atom. Crudely, we may say that its "grabbing power" is greater than that of the oxygen atom. Since no hydrogen atom ever holds more than one atom of any other element, it is used as the *standard in the study of valence*. *That property of an atom which indicates the number of hydrogen atoms with which it can combine, or which it may displace, is called its valence.*

**132. Kinds of Valence.** An element, such as chlorine, whose atom has the capacity for holding just one hydrogen atom is said to be *uni*-valent. An element like oxygen whose atom can hold two hydrogen atoms is said to be *bi*-valent. Elements having a valence of three are *tri*-valent; of four, *quadri*-valent; of five, *quinqi*-valent; of six, *hexa*-valent. No element is known that has a higher valence than eight (*octa*-valent).

**133. How Valence is Applied in Binary Compounds.** We have learned that a binary compound contains two elements only. We know that chlorine is univalent, since it combines with hydrogen, atom for atom. Oxygen is bivalent, since one oxygen atom can hold two hydrogen atoms. In the same manner, from the compound ammonia,  $\text{NH}_3$ , we learn that nitrogen has a valence of three. From the compound methane,  $\text{CH}_4$ , we learn that carbon has a valence of four.

Chemists have used different expressions, such as "bonds," "tubes of force," "links," "hooks," and "grabbing power," in their efforts to represent chemical affinity. Sometimes the valence of an element is represented graphically as follows:



Each line or "bond" represents a valence of 1, and these diagrams show that chlorine can hold 1 hydrogen atom; oxygen, 2; nitrogen, 3; and carbon, 4. The number of "bonds" an atom has tells us nothing concerning the *stability* of the compounds it forms. Ammonia, for example, although the nitrogen in it has three valence "bonds," is not so stable as hydrogen chloride, in which chlorine has but one. Valence is a measure of capacity, but not of strength or stability.

Some elements do not unite with hydrogen directly, but such elements almost always unite with oxygen. We may use oxygen as a standard in such cases, calling its valence 2. Examples of such compounds include  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SnO}_2$ . Since it takes two atoms of sodium to combine with one of oxygen, the valence of sodium must be 1. Calcium unites with oxygen, atom for atom; hence its valence

Na	⚡	O	ge of electricity. The letter $\epsilon$
Na	⚡	O	electron. (See Section 22.) An el
S	⚡	O	ctron only has a positive valence of
	⚡	O	um, Mg, can lose two electrons, an
	⚡	O	of 2. ( $\text{Mg}^0 - 2\epsilon = \text{Mg}^{++}$ .) Th
Al	⚡	O	depends upon the number of electron
	⚡	O	of such a metal seems to deper
	⚡	O	it parts with its electrons.
Al	⚡	O	e drawn by Thomson, we have th
Al	⚡	O	hich are greedy for electrons. The
	⚡	O	stand alone, but they readily "bo
	⚡	O	ns. When the chlorine atom, f
Al	⚡	O	on, it acquires a negative charg
	⚡	O	ne, therefore, has a negative valen

FIG. 96. — is capable of gaining two electron  
valence of 2. ( $\text{O}^0 + 2\epsilon = \text{O}^{=}$ .) Th

is 2. Aluminum, Al, has enent depends upon the number o  
valence of 4. Sometimes  
valence more clearly. (See In 1913, a brilliant young Eng

In writing formulas, it is customary to write first the symbol of the metallic element and follow it with the symbol of the non-metal. In any binary compound, the total number of "bonds" of the metallic element must exactly equal the total number of "bonds" of the non-metallic element. To illustrate, we may use the formula  $\text{Al}_2\text{O}_3$ . Let us write the symbol of each element, using accent marks to indicate its valence as follows:  $\text{Al}''' \text{O}''$ . The elements cannot combine atom for

atom. We see at a glance that 6 is the smallest multiple of both 2 and 3. Each element must have a total of 6 "bonds." Therefore we shall need 2 aluminum atoms of 3 "bonds" each and 3 oxygen atoms of 2 "bonds" each. Thus we find the formula for aluminum oxide to be  $\text{Al}_2''' \text{O}_3''$ . *The product of the number of atoms of one element times its valence equals the product of the number of atoms of the other element times its*

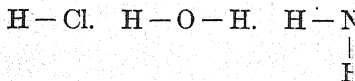
*valence.*

**133. How Valence is Applied in** We have learned that a binary compound only. We know that chlorine is united with hydrogen, atom for atom. Oxygen atom can hold two hydrogens in this manner, from the compound ammonia. Nitrogen has a valence of three. From methane,  $\text{CH}_4$ , we learn that carbon has a valence of four.

Chemists have used different expressions for their efforts to represent chemical valence of an element is represented by the number of bonds it forms.

*valence.*

Some students learn more quickly the following method of criss-crossing valences:  $\text{Al}^{\text{III}}\text{O}^{\text{II}}$  or  $\text{P}^{\text{V}}\text{O}^{\text{II}}$ . The valence and the number of atoms needed to balance the compound are just reversed. By the use of this method we get  $\text{Sn}^{\text{IV}}\text{O}^{\text{II}}$  instead of  $\text{SnO}_2$ . When the numbers are even we must simplify by reducing the numbers to their lowest terms.



Each line or "bond" represents the valence of the elements (inside front cover) he should be able to write the formula for any binary compound. For example, magnesium has a valence of 2. The formula for its oxide is  $\text{MgO}$ ; it cannot be  $\text{Mg}_2\text{O}_3$ ,  $\text{Mg}_2\text{O}$ , or  $\text{MgO}_2$ . Keeping in mind the fact that the valence of chlorine in all chlorides is 1, we write respectively the formulas for the chlorides of sodium, magnesium, aluminum, and tin as follows:  $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{AlCl}_3$ , and  $\text{SnCl}_4$ .

**134. The Electron Theory of Valence.** The modern theory of valence assumes that the force of attraction between atoms is electrical. J. J. Thomson suggests that some elements — namely, hydrogen and the metals may *lose* one or more electrons. (See Fig. 97.) The hydrogen atom is generous and loses one electron. The hydrogen atom has no electrical charge until it loses an electron. If we subtract an electron from it ( $H^0 - e = H^+$ ), the hydrogen atom then acquires a positive charge of electricity. The letter  $e$  is used to represent one electron. (See Section 22.) An element that can *lose one electron only* has a *positive valence of 1*. An element like magnesium, Mg, can lose *two* electrons, and have a positive valence of 2. ( $Mg^0 - 2e = Mg^{++}$ .) *The positive valence of a metal depends upon the number of electrons it can lose.* The activity of such a metal seems to depend upon the ease with which it parts with its electrons.

To complete the picture drawn by Thomson, we have the non-metallic elements, which are *greedy* for electrons. They have no charge as they stand alone, but they readily “borrow” or “pilfer” electrons. When the chlorine atom, for example, gains an electron, it acquires a negative charge. ( $Cl^0 + e = Cl^-$ .) Chlorine, therefore, has a negative valence of 1. The oxygen atom is capable of gaining two electrons; hence it has a negative valence of 2. ( $O^0 + 2e = O^{--}$ .) *The negative valence of an element depends upon the number of electrons it “borrows.”*

**135. Atomic Numbers.** In 1913, a brilliant young English chemist, H. G. J. Moseley, who later lost his life in the World War, was able by means of the X-ray spectra from different metals to determine the number of excess protons in the nuclei of different atoms.<sup>1</sup> (See Fig. 98.) He found that hydrogen has only one excess proton, and he assigned to hydrogen the *atomic number 1*. Helium has the atomic

<sup>1</sup> NOTE. Some other views of the structure of the atom are given in Chapter 40.

number 2; lithium is 3; beryllium is 4; boron, 5; carbon, 6; nitrogen, 7; oxygen, 8; and fluorine, 9. The atomic numbers of the other elements are given in the table on page 433.

Since the atom is electrically neutral, and the atomic number is equal to the *excess* protons or positive charges on the nucleus, it follows that the atomic number must also be equal to the number of planetary electrons surrounding the



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FIG. 98.—H. J. G. Moseley was a young English chemist who was killed in the trenches during the World War. He is known because of his work in determining atomic numbers.

nucleus. According to Dr. Bohr's theory of the planetary electrons, we may represent some of the lighter atoms as shown in Fig. 99.

The circle in the center represents the nucleus of the atom and the number inside shows the atomic number, or excess protons. The small black dots represent electrons. They seem to be grouped in rings, or concentric spheres or shells, as represented by the dotted lines.

### 136. How Compounds

**Are Formed.** It seems,

then, as if compounds are formed by elements which lose electrons and thus become positively charged, uniting by electrical attraction with those elements which gain electrons and become negatively charged. In the accompanying diagram (see Fig. 100), we have represented what is believed to occur when hydrogen combines with fluorine. Hydrogen loses one electron and becomes positively charged. The electron lost by the hydrogen is gained by the fluorine atom, thus charging it negatively. As John



Mills explains in his *Letters of a Radio Engineer to His Son*, the hydrogen electron has no playfellows. So this lonely electron strolls over to join the seven fluorine electrons in

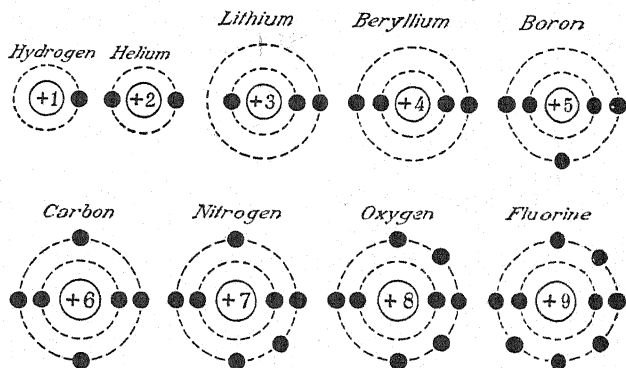


FIG. 99. The hydrogen atom has a single electron. In this group of atoms the number increases to nine.

whatever game they are playing. But this electron is still attracted to the parent nucleus, and the two oppositely charged atoms then unite to form the compound hydrogen fluoride, HF. Metals do not ordinarily combine with one another, because they all tend to lose electrons and become positively charged. We learned in Section 22 that charges of the same sign repel. For the

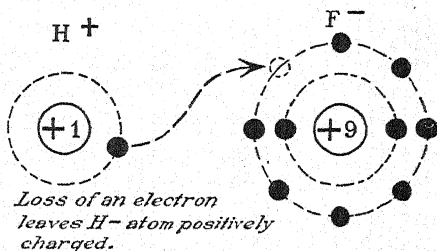


FIG. 100. — The hydrogen atom unites chemically with the fluorine atom.

same reason two non-metallic elements show little chemical affinity for one another, since such elements are likely to be charged with electricity of negative sign. For some reason elements seem to be trying to complete rings or shells of eight

electrons, although the first ring is complete with two electrons. If we observe the diagram that represents the helium atom, we find that there are two electrons. No element is able to take any electrons from helium, nor does helium ever gain any electrons. Its charge is always zero. Therefore it forms no compounds whatever. It preserves the spirit of the Monroe Doctrine and forms no entangling alliances. We

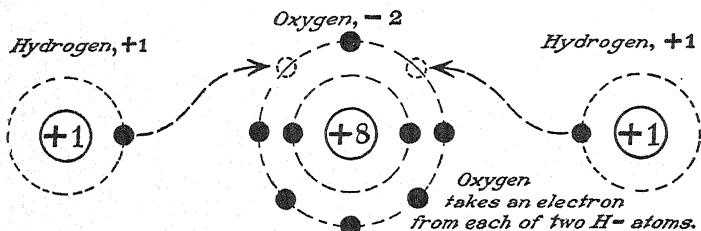


FIG. 101.— Since oxygen has a negative valence of two, it combines with two positively charged hydrogen atoms.

observe that lithium has three planetary electrons, but two of those electrons are in the inner shell and cannot be detached. Lithium has only one *valence electron*. It readily loses that electron, and becomes an active univalent positive element. Beryllium has four electrons; two of them are in the inner stable ring or shell; it has *two valence electrons*. Boron has three valence electrons.

If we examine the configuration for oxygen, we find that it has eight electrons. Two are stable. It is conceivable that oxygen might lose six electrons, but it is much more plausible to expect that it will take two electrons from some other element to complete its ring or shell of eight. Figure 101 shows what may occur when hydrogen and oxygen unite to form water. It takes two hydrogen atoms, each having one electron, to supply the electrons for one oxygen atom. In such compounds, it is probable the atoms *share* electrons.

In the formation of ammonia, the nitrogen atom needs

three electrons to complete a ring of eight. Hence it takes three hydrogen atoms to furnish the three electrons shared

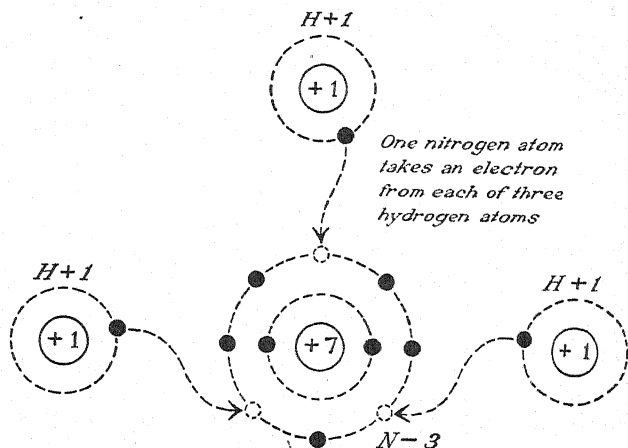


FIG. 102. — The nitrogen atom combines with three hydrogen atoms.

with the nitrogen atom. That is the reason why ammonia has the formula NH<sub>3</sub>. (See Fig. 102.)

**137. Atoms with Ten or More Electrons.** The neon atom has ten electrons, two in an inner ring or shell, and eight in another. (See Fig. 103.) This configuration is stable, and no electrons can be added to it or taken from it. Hence neon belongs to that bachelor group of elements that forms no alliances with other elements. The sodium atom has eleven planetary electrons, two in one ring, eight in another, and a single valence electron. It is a very active metal, since it loses this single electron so easily. The chlorine atom has an inner ring of two electrons, a second ring of eight, and seven valence electrons.

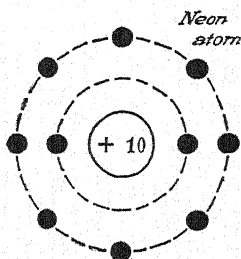


FIG. 103. — The neon atom neither gains nor loses electrons.

Because of its greed for an extra electron, it is one of the most active non-metals known. The following diagram shows how a sodium atom is believed to lose an electron to a chlorine atom, and combine with the atom to form a molecule of sodium chloride,  $\text{NaCl}$ . (See Fig. 104.)

**138. Valence of Radicals.** It would seem as if the valence might be more difficult to determine when there are three or more elements in a compound. This may be true, but in the majority of such cases two of the elements in such a compound form a *radical*. In a radical two or more elements

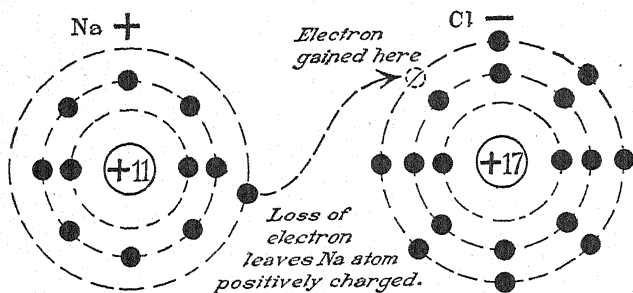
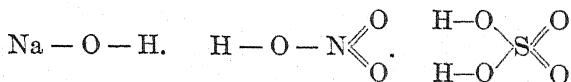


FIG. 104. — The positively charged sodium atom unites chemically with the negatively charged chlorine atom.

may act as one. A radical may be defined as a group of elements that generally acts as a single element. In the compound sodium hydroxide,  $\text{NaOH}$ , the group  $(\text{OH})$  is a radical. In sulfuric acid,  $\text{H}_2\text{SO}_4$ , the  $(\text{SO}_4)$  group is a radical. The compound nitric acid,  $\text{HNO}_3$ , contains the radical  $(\text{NO}_3)$ . Since in a radical the two elements act like a single element, we can find the valence of a radical in exactly the same manner that we determined valence of elements in binary compounds. For example, the  $(\text{OH})$  radical has a valence of 1; the  $(\text{SO}_4)$  radical has a valence of 2, since it unites with 2 atoms of hydrogen to form sulfuric acid; the  $(\text{NO}_3)$  group has a valence of 1.

Suppose we desire to write the formulas for the hydroxides of the various metals mentioned in Section 133. Calcium hydroxide is  $\text{Ca}(\text{OH})_2$ ; aluminum hydroxide is  $\text{Al}(\text{OH})_3$ ; and tin hydroxide is  $\text{Sn}(\text{OH})_4$ . The sulfates of these metals have the following formulas:  $\text{Na}_2\text{SO}_4$ ;  $\text{CaSO}_4$ ;  $\text{Al}_2(\text{SO}_4)_3$ ; and  $\text{Sn}(\text{SO}_4)_2$ .

That the oxygen in a ternary compound usually holds in combination all the other elements may be seen from the following structural formulas:



The student will soon learn the valence of the more common radicals. The majority of them combine with hydrogen, and their valence can be found from some formula with which the student is familiar. For example, no one can forget that the formula for sulfuric acid is  $\text{H}_2\text{SO}_4$ . Then he can apply this knowledge to the dozen or more sulfates he may study, all of which have one or more sulfate  $(\text{SO}_4)^=$  radicals.

**139. Some Atoms Have Variable Valences.** The study of valence would be much easier if no element ever varied in valency. But some elements are quite fickle. For example, the mercury atom may lose one electron and have a valence of 1. ( $\text{Hg}^0 - \epsilon = \text{Hg}^+$ .) In the compound mercurous chloride,  $\text{HgCl}$ , the mercury has a valence of 1. But under different conditions, the mercury atom may lose two electrons. ( $\text{Hg}^0 - 2\epsilon = \text{Hg}^{++}$ .) In such a case mercury has a valence of 2, and may form the compound mercuric chloride,  $\text{HgCl}_2$ . There are two chlorides of mercury. To distinguish them, we call that one in which the metal has the lower valence mercurous; the one in which the mercury atom has the higher valence is called mercuric.

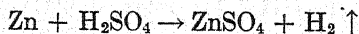
Iron forms two classes of salts in which the valence of the iron varies. In the compound ferrous oxide,  $\text{FeO}$ , the valence

of the iron is 2. In the compound ferric oxide,  $\text{Fe}_2\text{O}_3$ , the valence of the iron is 3. If we look over the list of elements given on the inside of the front cover, we find that the valence of some elements never seems to vary. In some cases, the valence varies widely.

Such elements as hydrogen, sodium, potassium, calcium, and many other metals seem to be always electro-positive. On the other hand, such elements as fluorine, chlorine, bromine, and oxygen seem practically always to be electro-negative. But an element, such as carbon, could lose four electrons to form a stable configuration, or it could gain four. It appears that in the compound  $\text{H}_4\text{C}$ , the carbon atom must have taken four electrons from four hydrogen atoms, and that in the compound  $\text{CO}_2$  it must have lent four electrons to two oxygen atoms. There is considerable evidence to support the theory that in both these compounds the two elements *share* electrons in what is called *co-valence*. This topic will be more fully discussed in a later chapter.

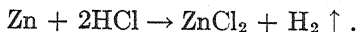
Another interesting example of variable valence may be shown by the study of three compounds of sulfur. In the compound hydrogen sulfide,  $\text{H}_2\text{S}$ , the sulfur atom has a valence of  $-2$ . In the compound sulfur dioxide,  $\text{SO}_2$ , its valence seems to be  $+4$ ; and in the compound sulfur trioxide,  $\text{SO}_3$ , the valence of the sulfur atom seems to be  $+6$ .

**140. The Relation of Valence to Substitution.** Just as it is impossible to have 1 atom of a bivalent element combine with *only* 1 atom of a univalent element, so do we find it impossible to substitute one atom of a bivalent element for *only* 1 atom of a univalent element. For example, if we write the equation for the interaction of zinc and sulfuric acid, we have the following:

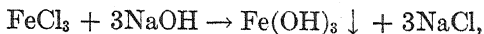


The zinc element is bivalent, and substitutes itself for 2 atoms of univalent hydrogen. When the acid used is hydrogen

chloride, or hydrochloric acid, then we must take 2 molecules of hydrogen chloride in order to have the 2 hydrogen atoms for which the zinc may be substituted. The equation follows:



In double substitution, too, we must consider valence. In the following equation,



we must use three molecules of sodium hydroxide to get the three univalent sodium atoms to be substituted for one trivalent iron atom. At the same time, we get three univalent (OH) radicals to combine with the trivalent iron.

**141. Valence Is a Useful Working Tool.** Chemists have spent much time in trying to explain "why" and "how" atoms unite. But, after all, it seems even more important to know that they do unite. The valence scheme is a valuable tool for the chemist. He learns the valences of the important elements, instead of trying to memorize the formulas for thousands of compounds. When he knows the valence, he can write the formulas for compounds, even for those with which he is unfamiliar.

The beginner needs to be cautioned against expecting too much from the valence scheme. He may write formulas, for example, of compounds that do not exist. Then he will find many compounds that are puzzling, such as  $\text{H}_2\text{O}_2$ ,  $\text{CaC}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{H}_4$ . The student should memorize the valences of all the common elements, and the valences of the most common radicals. He will find valence useful in many ways, but he must not expect it to prove a panacea for all the ills of the chemist.

**142. Table of Valences.** To familiarize the student with the valences of the most common elements, a table is given here for use in the questions at the end of the chapter. The elements that have variable valences appear in two or



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more of the columns. In writing formulas, it will be helpful to the beginner if he writes the positive and negative signs after each element and radical to indicate the proper valence.

EXAMPLES.  $\text{Ca}^{++}(\text{CO}_3)^{-}$ ;  $\text{As}_2^{+++}\text{S}_3^{-}$ ;  $\text{Mg}^{++}\text{O}^{-}$ ;  $\text{Al}^{+++}(\text{PO}_4)^{-}$

TABLE OF VALENCE

One	Two	Three	Four	Five	Six
Cl, H, I, Hg, Ag, Na, K	Ca, Cu, Fe, Mg, Hg, O, Sn, Zn, S	Al, Fe, N, P	C, Si, S, Sn	N, P	S

VALENCE OF COMMON RADICALS. (All but one are negative radicals.)

One	Two	Three
OH, NO <sub>3</sub> , ClO <sub>3</sub> , NH <sub>4</sub> (positive), NO <sub>2</sub> , MnO <sub>4</sub>	SO <sub>4</sub> , CO <sub>3</sub> , SO <sub>3</sub> , CrO <sub>4</sub>	PO <sub>4</sub> , PO <sub>3</sub> , BO <sub>3</sub>

## SUMMARY

That property of an element which indicates the number of hydrogen atoms with which its atom can combine, or which it may displace, is called its *valence*.

Elements vary in valence from 1 to 8. Hydrogen and the metals are electro-positive; oxygen and other non-metals are usually electro-negative. In writing formulas, it is customary to write the electro-positive element first.

A binary compound has two elements. To write the formula for a binary compound, one must know the valence of both elements. Next we write the symbols in order, the positive element first, with the proper number of electrical charges indicated by plus and minus signs just above and to the right of each symbol. Then take such a number of atoms of each that the total number of positive charges will just equal the total number of negative charges.

In ternary compounds, two of the elements generally act as radicals. A radical is a group of elements that behaves as a single

element. In the writing of formulas, they are treated as if they were a single element.

An atom that can lose electrons acquires a positive charge. Some atoms gain, or take, electrons and acquire a negative charge. The activity of an element depends upon the ease with which it gains or loses electrons.

The concept of atomic numbers was developed by Moseley. Each atom has a number that depends upon the number of excess protons in its nucleus. The atomic number of an element is also equal to the number of planetary electrons surrounding the nucleus of its atom.

Compounds are believed to be formed by the attraction of oppositely charged atoms. Atoms that have rings of 2 or 8 electrons are *stable*. They do not form compounds. Other atoms seem to be trying to form rings of eight electrons, either by losing or by gaining electrons.

Some atoms have variable valences. Valence also applies in substitution reactions.

## QUESTIONS

1. Write the formulas for all the oxides of the following metals: K, Cu, Mg, Ag, and Zn.
2. Write the formulas for two oxides of each of the following elements, and write the name of each compound: Fe, Sn, Hg, N, and P.
3. Write the formulas for the hydroxides of all the elements given in question 1.
4. Write the formulas for two sulfates of the following: Fe, Sn, and Hg.
5. Write the formulas for the sulfate, nitrate, chloride, hydroxide, and phosphate of ammonium,  $\text{NH}_4$ .
6. Write the formulas for the permanganates of sodium and potassium. (Permanganates have one or more  $\text{MnO}_4$  radicals.)
7. In what two ways can you determine the valence of a radical?
8. Which element do you think can form more compounds, one of a single valence, or one whose valence is variable?

9. Name several elements that are generous and part with their electrons easily.

10. Name several elements that are greedy for electrons.

11. Why is the valence of an element never more than eight?

12. In the top row of the following table certain elements and radicals are given with their valence indicated. In the left-hand column a number of metals is listed. Copy the table and fill in the formulas for all the compounds as shown for the sodium compounds.

	Oxides	Hydrides	Chlorides	Nitrates	Sulfates	Phosphates	Carbonates
	O =	(OH)⁻	Cl⁻	(NO₃)⁻	(SO₄)⁻	(PO₄)⁻	(CO₃)⁻
Na⁺	Na₂O	NaOH	NaCl	NaNO₃	Na₂(SO₄)	Na₃(PO₄)	Na₂(CO₃)
K⁺							
Hg⁺							
Ag⁺							
Ca⁺⁺							
Cu⁺⁺							
Fe⁺⁺⁺							
Mg⁺⁺							
Al⁺⁺⁺							
Pb⁺⁺							
Fe⁺⁺							
Zn⁺⁺							
⁺⁺							
Sn⁺⁺							

## CHAPTER 13

# CHEMICAL EQUATIONS AND CHEMICAL PROBLEMS

### Vocabulary

**Equation.** An expression that shows by the use of symbols and formulas what occurs during a chemical reaction.

**Factor.** One of the elements or compounds entering into a chemical reaction.

### A. EQUATIONS

**143. What is an Equation?** In several of the reactions that we have studied, *word* equations have been used to help explain what chemical changes took place. The *formula* equations, which were printed without full explanation, really show to the chemist exactly what happens during such changes. Now that we know the full significance of formulas and how to write them by the aid of valence, we may study the meaning of formula equations and learn how to write them ourselves.

On the *left* side of the equation, we write the formulas for all the *factors*; this includes the symbols of all the elements and the formulas for all the compounds that enter into the reaction. On the *right* side of the equation, we write the symbols and formulas of all the elements and compounds that are formed as *products* upon the completion of the reaction. An equation shows what actually happens as a result of chemical action. *It is not a prophecy, but a statement of fact.* It is more explicit than a word equation, and considerably briefer.

A chemical equation has no value unless it is correct in all respects:

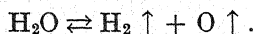
1. *It must represent the facts.* Before one can write an equation he must know all the *factors* and all the *products*. This means he must know with what chemicals he started, and also what products he has at the end of the reaction. The chemist relies upon analysis for such facts.

2. *Every compound in the equation must be balanced with respect to the valence of its elements and radicals.* To complete this second step in writing equations, a *student must know the valence of each element*. Then he proceeds, by the methods given in Chapter 12, to write the correct formula for all the compounds.

3. *There must be the same number of atoms on each side of the equation.* This is a matter of simple arithmetic. No atoms are lost during a chemical change, and every one must be accounted for. Atoms are not manufactured during a chemical change, and the products cannot have more atoms than the factors. *The student may use as many molecules as are necessary to balance the equation.*

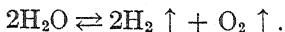
4. *In a molecular equation, every elementary gas must contain two atoms.* In Section 124, it was proved that gaseous elements have two atoms per molecule. This step is especially important when dealing with *volume relations*.

**144. How to Write Equations.** Since one learns by doing, to use the words of Squeers, let us study some of the equations where the facts have already been learned. We decomposed water to prepare hydrogen and oxygen. Water is the only *factor*, and the *products* are hydrogen and oxygen. Thus we write the equation, using symbols and formulas:

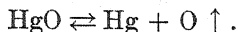


Such an equation appears to be correct, since it tells the truth, every compound is correctly balanced as to valence, and no atoms have been gained or lost. But we have forgotten that *the molecule of an elementary gas contains two atoms*. To obtain the two atoms of oxygen needed, we must

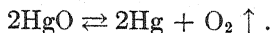
use two molecules of water; in other words, the above equation must be multiplied by two throughout. The following equation is correct in every respect:



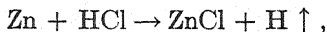
In the decomposition of mercuric oxide by heat, we have the following:



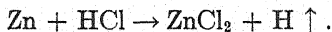
This equation is correct in three respects, but the elementary gas oxygen must have two atoms. Hence we use double the number of atoms of each compound and each element to form the molecular equation. Mercury is an element, but not a gas. Hence we write  $2\text{Hg}$ , instead of  $\text{Hg}_2$ .



Let us next take up the study of an equation where substitution occurs. When hydrogen chloride in water solution is added to zinc, the zinc displaces the hydrogen, which is set free as a gas. The other product formed is zinc chloride. If we write the equation as shown below,

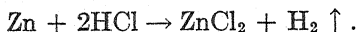


we find by checking it that it is *not* correct. It appears to be correct as to fact, but since zinc is bivalent, the formula for zinc chloride is  $\text{ZnCl}_2$ . The next step is to change our equation as follows:



Now the facts are as represented and every compound is balanced as to valence, but there are more atoms on the right side of the equation than on the left. In other words, it is not an equation. We need *another chlorine atom*. If we were to write hydrogen chloride  $\text{HCl}_2$ , that would give the needed chlorine atom, but hydrogen cannot hold two

chlorine atoms. One of the most common mistakes made by the beginner is that of destroying the balance of a compound in order to get the required number of atoms. He must keep this sequence in mind: (1) The facts. (2) Every compound properly balanced. Then *he must not change the subscript numbers after this step is completed.* But *he can use as many molecules as are needed to get the required number of atoms.* In this case, he may use two molecules of hydrogen chloride,  $2\text{HCl}$ , and then the equation becomes,



*Check.* The equation states the facts; every element in every compound has the proper valence; no atoms have been gained or lost; and every molecule of an elementary gas has two atoms. If the student will always *check* his equations in this manner, he will have little difficulty in writing equations.

Let us next consider a metathesis reaction. If we add a solution of silver nitrate to a solution of sodium chloride, double decomposition occurs, and silver chloride and sodium nitrate are formed. The equation, with the plus and minus signs shown, follows:



In such equations the student must remember that it is customary to write the symbol for the positive element first. This is usually hydrogen or some metal. We would no more expect two positive elements to combine than we would expect to see two boys dance away together at a mixed dance. We do not have such compounds as  $\text{AgNa}$  or  $\text{ClNO}_3$ . This is what actually happens: *The silver atom and the sodium atom exchange places.* We shall be safe in assuming that in double decomposition reactions, if any change occurs at all, one positive (metallic) element will be substituted for



another positive element, and it will combine with a negative (non-metallic) element, or a non-metallic radical. *Radicals usually remain intact during chemical reactions.*

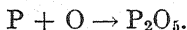
**145. Some Equations That Are More Difficult.** In the laboratory preparation of oxygen, we learned that oxygen may be prepared by the heating of potassium chlorate,  $\text{KClO}_3$ . The equation follows:



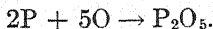
But we must not forget that the oxygen molecule contains two atoms. We obtain three oxygen atoms, or enough for  $1\frac{1}{2}$  molecules, from one molecule of potassium chlorate. If we start with 2 molecules of potassium chlorate, then we can do away with fractional molecules. The equation then becomes,



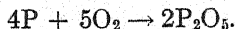
When a substance burns it unites with oxygen. In the burning of phosphorus, the compound formed is  $\text{P}_2\text{O}_5$ . The first step in writing the equation follows:



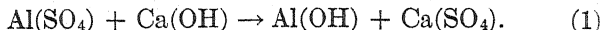
This expresses the fact that phosphorus combines with oxygen and forms phosphorus pentoxide,  $\text{P}_2\text{O}_5$ , a properly balanced compound. But we need more phosphorus and oxygen atoms as shown in the second step:



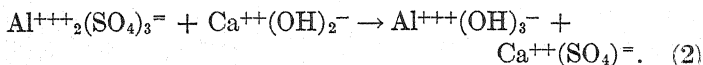
But oxygen is an elementary gas, and the 5 oxygen atoms furnish enough oxygen to form only  $2\frac{1}{2}$  molecules. To avoid the use of fractional molecules, we must double the entire equation. Then it becomes correct in all respects:



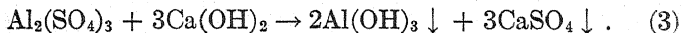
Let us take one more type equation, the one used in the coagulum process of water purification. We may use the following steps: (1) to represent fact.



The student will observe that the two metallic elements exchange places. We have enclosed the radicals in parentheses. Step 2 consists in balancing all the compounds so each element and radical will have the correct valence.



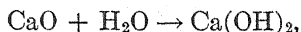
From the formula for aluminum sulfate we observe that there are enough aluminum atoms to form two molecules of aluminum hydroxide, and enough  $\text{SO}_4$  groups to form three molecules of calcium sulfate. Hence in the following step (3) we write the coefficients 2 and 3 before those molecules respectively. Next we observe that we need three atoms of calcium for the three molecules of calcium sulfate. We can get those atoms only by taking three molecules of calcium hydroxide. The completed equation follows:



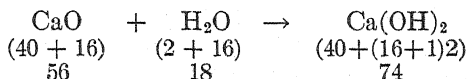
## B. CHEMICAL ARITHMETIC

**146. Problems Relating to Equations.** Since no atoms are gained or lost during a chemical reaction, and atoms have a definite weight, then it must follow that the relative weights of factors and products as represented by a *balanced* equation may be calculated. Three types of problems pertaining to equations may be given: (1) *Weights may be given and weights required.* (2) *Weights may be given, and volumes required; or volumes given and weights required.* (3) *Volumes given and volumes required.*

147. How Relative Weights Are Calculated. If we study the simple equation,



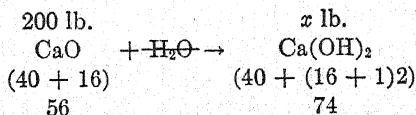
we see that one molecule of calcium oxide unites with one molecule of water to form one molecule of calcium hydroxide. But let us write below each formula the molecular weight of that particular compound, as shown below:



It is evident that 56 *parts by weight* of calcium oxide unite with 18 *parts by weight* of water to form 74 *parts by weight* of calcium hydroxide. What do we mean by *parts by weight*? We mean that 56 gm. of calcium oxide will unite with 18 gm. of water; or we mean that 56 lb. of calcium oxide will unite with 18 lb. of water. When we start with grams of one compound, the relative weights of the others will be in grams. If we start with pounds, ounces, or tons of one compound, the other compounds will have a corresponding denomination.

PROBLEM. Given 200 lb. of calcium oxide. How many pounds of calcium hydroxide can be formed by slaking this oxide in water?

SOLUTION. (1) Let us write the equation. (2) Just above the formula for the compound given let us write the actual weight, 200 lb.; and above the formula for the compound required we write the required weight,  $x$  lb. (3) Under each formula let us write the corresponding molecular weight as found by *adding* (*never multiplying*) the atomic weights. (4) Form a proportion as follows: ACTUAL WEIGHT OF KNOWN COMPOUND : ACTUAL WEIGHT OF UNKNOWN COMPOUND = MOLECULAR WEIGHT OF KNOWN COMPOUND : MOLECULAR WEIGHT OF UNKNOWN COMPOUND.

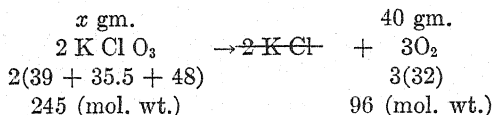


## 200 CHEMICAL EQUATIONS, CHEMICAL PROBLEMS

From the steps as outlined, we have the following proportion:  $200 : x = 56 : 74$ . Whence,  $x = 264.3$ , the number of pounds of calcium hydroxide that would be formed. The amount of water needed was not a part of our problem, so we *cancel* that formula after the equation is balanced, or neglect it entirely. Let us use the same steps in solving a second type problem.

**PROBLEM.** If we need 40 gm. of oxygen for an experiment, how many grams of potassium chlorate must be heated to liberate the oxygen?

**SOLUTION.** Let us proceed just as we did in the preceding problem. (1) The equation. (2) Actual weights. (3) Molecular weights. (4) The proportion.



By proportion,  $x : 40 = 245 : 96$ ; whence,  $x = 102.1$  gm. Here we omit the potassium chloride, since it is not a part of our problem. If we were asked to find how many grams of potassium chloride are formed, then we would use the molecular weight of that compound.

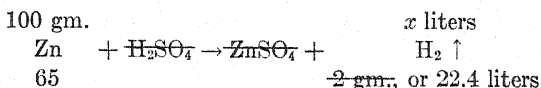
**NOTE.** It is desirable to make a preliminary estimate in problems of the type we have just solved. In the first one, for example, we note that the molecular weight of the calcium hydroxide is approximately 30% more than that of the calcium oxide. Hence the answer will be about 30% more than the 200 lb. with which we started. In the second case, we see that it takes about 2.5 gm. of potassium chlorate to liberate 1 gm. of oxygen. Hence it will take about 100 gm. to set free 40 gm. of oxygen.

★ **148. How to Solve Problems Involving both Weight and Volume Relations.** Problems of this type are not so common as those just studied, but we sometimes need to know how many grams of a substance are needed to liberate a given volume of a gas, or vice versa. In solving this type of

problem, it will be well to keep in mind the fact that *one mole of any gas occupies 22.4 liters.*

PROBLEM. How many liters of hydrogen will be set free by the action of an excess of sulfuric acid on 100 gm. of zinc?

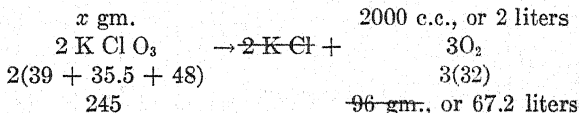
SOLUTION. The steps are as follows: (1) Write the equation. (2) Write the actual weight of zinc given (100 gm.) above its symbol, and the required volume of hydrogen ( $x$  liters) above its symbol. (3) Then write beneath the corresponding formulas the molecular weights. BUT INSTEAD OF THE ONE MOLE OF HYDROGEN (2 gm.) WE USE ITS EQUIVALENT, WHICH IS 22.4 LITERS. (4) Then we may form a proportion in which actual weight : liters = molecular weight : liters.



From the proportion,  $100 : x = 65 : 22.4$ , we find that  $x = 34.2$  liters. We may cancel out the unused formulas,  $\text{H}_2\text{SO}_4$  and  $\text{ZnSO}_4$ , and the 2 gm., for which we have substituted 22.4 liters.

PROBLEM. How many grams of potassium chlorate must be heated to prepare five 400-c.c. bottles of oxygen gas at S. T. P.?

SOLUTION. (1) Write the equation. (2) Above the formula for the potassium chlorate write the number of grams required ( $x$  gm.); above the formula for the oxygen write the number of liters (2000 c.c., or 2 liters). (3) Below the corresponding formulas write the molecular weights of potassium chlorate and oxygen. Substitute for the 3 moles (96 gm.) of oxygen its equivalent (67.2 liters). Each mole occupies 22.4 liters. (4) Form the proportion and solve for  $x$ .

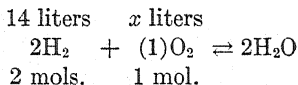


In the proportion,  $x : 2 = 245 : 67.2$ , we find that  $x = 7.29$ , the number of grams of potassium chlorate needed. Of course *volume relations apply to gases only.*

**149. Problems Where Volumes Are Given and Volumes Required.** The application of Avogadro's Law makes this type of problem the simplest of all. It is most important that the molecular equation be correctly written so that each elementary gas has two atoms per molecule. The coefficients in such molecular equations will be proportional to the volumes of the gases at S. T. P. It is unnecessary to use atomic or molecular weights.

**PROBLEM.** How many liters of oxygen will be needed for the complete combustion of 14 liters of hydrogen?

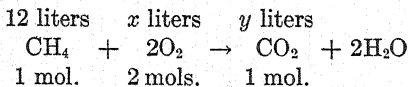
**SOLUTION.** (1) Write the molecular equation. (2) Write the numbers representing the gas volumes above the corresponding formulas. (3) Write below the formulas the coefficient of each (number of molecules). (4) Form a simple proportion between the relative volumes and relative coefficients. (By Avogadro.)



Then, 14 liters :  $x$  liters = 2 mols. : 1 mol.; whence,  $x$  equals 7 liters, the volume of oxygen needed.

**PROBLEM.** How many liters of oxygen are needed for the complete combustion of 12 liters of marsh gas,  $\text{CH}_4$ ? How many liters of carbon dioxide are formed?

**SOLUTION.** (1) Write the equation. (2) Write the numbers representing the gas volumes above the corresponding formulas. (3) Write below the formulas the coefficient of each one. (4) Form the proportion.



To find the number of liters of oxygen, we use the proportion,  $12 : x = 1 : 2$ ; whence,  $x = 24$ , the number of liters of oxygen needed to unite with 12 liters of marsh gas. To find the number of liters of carbon dioxide, we use the proportion,  $12 : y = 1 : 1$ . Whence,  $y = 12$  liters. When comparing relative gas volumes,

we always find their ratio to be the same as the ratio of the coefficients of the molecules.

## SUMMARY

A chemical equation is a simple expression that shows what occurs when a chemical reaction takes place. On the left side of the equation, the *factors* are written. The *products* that are formed are written on the right side.

To be correct an equation must: (1) Be true to fact. (2) Have all compounds correctly balanced as to valence. (3) Account for all the atoms and no more. (4) Have two atoms per molecule for each elementary gas.

In writing equations, students should remember: (1) That metals and hydrogen are usually positive. (2) That positive elements are written first in a formula. (3) That the non-metals are usually negative. (4) That radicals usually remain intact during the reaction. (5) That subscripts are not to be changed after a compound is correctly balanced. (6) That as many molecules may be used as are necessary to supply the required number of atoms.

Three types of problems pertaining to equations are possible: (1) When weights are given and weights are required. (2) When weights are given and volumes required, or vice versa. (3) When volumes are given and volumes required. Of course volume relations always pertain to gases.

## EQUATIONS

(For reference and for use in solving problems)

1.  $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2 \uparrow$ .
2.  $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$ .
3.  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2 \uparrow$ .
4.  $\text{C} + \text{CO}_2 \rightarrow 2\text{CO} \uparrow$ .
5.  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ .
6.  $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2 \uparrow$ .
7.  $2\text{C}_2\text{H}_2 + 5\text{O}_2 \rightarrow 4\text{CO}_2 \uparrow + 2\text{H}_2\text{O}$ .
8.  $\text{BaO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 \downarrow + \text{H}_2\text{O}_2$ .
9.  $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{Ca}(\text{HCO}_3)_2$ .



## PROBLEMS

(Use approximate atomic weights)

## GROUP A

1. How many grams of oxygen can be prepared from 10 gm. of mercuric oxide?
2. How many grams of oxygen can be prepared from 10 gm. of potassium chlorate?
3. How many grams of zinc are needed to liberate 5 gm. of hydrogen from sulfuric acid?
4. How many grams of sodium chloride,  $\text{NaCl}$ , are needed to unite with 10 gm. of silver nitrate,  $\text{AgNO}_3$ , in water solution? How many grams of silver chloride will be precipitated? If the excess water is evaporated, how many grams of sodium nitrate will be left?
5. How many pounds of copper can be obtained from 200 lb. of copper oxide?
6. How many pounds of copper sulfate can be made from 300 lb. of copper?
7. How many pounds of iron are needed to set free 10 lb. of hydrogen from steam? (See equation No. 6, page 203.)
8. How many pounds of hydrogen peroxide are produced by the action of an excess of sulfuric acid on 45 lb. of barium peroxide?

## GROUP B

9. How many liters of oxygen can be prepared from 10 gm. of potassium chlorate?
10. How many grams of zinc are needed to prepare 5 liters of hydrogen from sulfuric acid?
11. How many liters of hydrogen will be needed to reduce 10 gm. of copper oxide to metallic copper?
12. How many grams of potassium chlorate are needed to prepare 9 moles of oxygen? To prepare 22.4 liters of oxygen?
13. How many liters of oxygen are needed to burn 5 liters of acetylene? How many liters of carbon dioxide will be formed?
14. How many grams of sodium will be needed to liberate 10 liters of hydrogen from water?

15. How many liters of carbon dioxide would be formed by burning 225 gm. (about half a pound) of carbon?

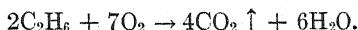
16. How many liters of carbon monoxide will be produced by the action of an excess of carbon dioxide on 40 gm. of carbon? (Equation 4.)

17. If 130 gm. of zinc interact with 150 gm. of hydrogen chloride, how many grams of zinc chloride will be formed. Hint: First calculate which is present in excess.

18. How many grams of silver chloride will be formed by the interaction of 100 gm. of silver nitrate with 80 gm. of sodium chloride?

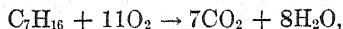
19. How many grams of potassium chlorate will be required to supply the oxygen needed to fill four 380-c.c. bottles when the temperature is 27° C. and the pressure is 720 mm.?

20. How many liters of oxygen will be needed to burn completely 60 liters of the gas ethane,  $C_2H_6$ , as shown by the following equation:



How many liters of carbon dioxide will be formed?

21. A sample of gasoline has the average formula  $C_7H_{16}$ . The following equation,



represents its complete combustion. Assuming that the gasoline vapor and oxygen both have the same temperature and pressure, how many liters of oxygen are needed to burn completely 100 liters of gasoline vapor? If air is 21% oxygen, what is the ideal adjustment of a carburetor designed to mix the air and gasoline vapor in the right proportion?

## CHAPTER 14

### ACIDS, BASES, AND SALTS

#### Vocabulary

**Indicator.** A substance used to determine by means of a color reaction the presence of an acid or a base.

**Lichen.** A flat, scale-like, flowerless plant.

**Neutralization.** The union of the positive element of an acid with the negative radical of a base to form water.

**Alkali.** A term applied to soluble bases; it also includes some compounds that are not bases, but act like them.

**Caustic.** A substance that burns or corrodes the tissues of the body.

**150. Introductory.** Several times it has been necessary to refer to some acid. Bases and salts have also been mentioned frequently. Of the various compounds mentioned in chemistry, many of them belong to one of the three following classes: *acids, bases, and salts*. We have used hydrochloric acid and sulfuric acid in the laboratory. From the experiment showing the behavior of sodium on water, we are familiar with the base sodium hydroxide,  $\text{NaOH}$ . Sodium chloride is typical of a large number of compounds known as *salts*. In this chapter we shall select certain representatives to show the method of preparation and the general characteristics of each of these three groups of compounds.

#### A. ACIDS

**151. Where Acids Are Found.** Several acids are found in nature, or are formed by natural processes. Green fruits contain acids, which often form salts as the fruits ripen. Such ripe fruits as the orange, lemon, and grape fruit contain acids. Fermentation often produces acids, such as *lactic*

*acid* in sour milk, or *acetic acid* in vinegar. Many acids are manufactured for industrial use.

**152. Three Important Acids.** There are three acids that are of such major importance that they may justly be called the triumvirate. These three acids, hydrochloric, nitric, and sulfuric, were known to the old alchemists. There are few industries that do not make use of one or more of these acids in quantity.

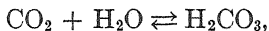
1. *Hydrochloric acid.* When hydrogen chloride,  $\text{HCl}$ , a heavy *gas*, is dissolved in water, the solution has acid properties. When we speak of acid properties we refer to certain chemical properties of acids that will be discussed in a subsequent section. The *pure acid* does not have those properties but a *water solution of the acid* does. When a chemist speaks of an acid, he nearly always refers to a water solution of the acid. *Concentrated hydrochloric acid* contains about 38% by weight of the gas, hydrogen chloride. *Ordinary dilute acid*, generally used in the laboratory, is made by adding 1 part of the concentrated acid to 4 parts of water. The water solution of the pure acid is colorless.

2. *Nitric acid.* This acid is a volatile liquid that has the formula  $\text{HNO}_3$ . The 100% acid is never put on the market, but the *concentrated nitric acid* of commerce contains 68% of nitric acid with 32% of water. This liquid is colorless when free from impurities. *Ordinary dilute nitric acid* is made by adding 1 part of the concentrated nitric acid to 5 parts of water.

3. *Sulfuric acid.* This acid, which has the formula  $\text{H}_2\text{SO}_4$ , is so important industrially that it has been called the "old horse of chemistry." It is a heavy, oily liquid that has a high boiling point. The *concentrated acid* contains about 93.5% of the acid and 6.5% of water. *Ordinary dilute sulfuric acid* is made by adding 1 part of the concentrated acid to 6 parts of water. CAUTION. *Never add water to the concentrated acid.*

**153. How Acids Are Prepared.** There are two more or less general methods of preparing acids. The first one was mentioned in the study of water.

1. *Non-metallic oxides and water.* We learned that carbonic acid may be prepared by dissolving carbon dioxide in water. The reaction represented by the equation,



is reversible. If we heat the carbonic acid,  $\text{H}_2\text{CO}_3$ , it will decompose into water and carbon dioxide. We have really *dehydrated* the acid. The carbon dioxide is called an *acid anhydride*. *The oxide of a non-metal that will combine with water and form an acid is called an acid anhydride.*

Sulfur trioxide,  $\text{SO}_3$ , is also an acid anhydride. When this compound is added to water, sulfuric acid is formed. The equation follows:

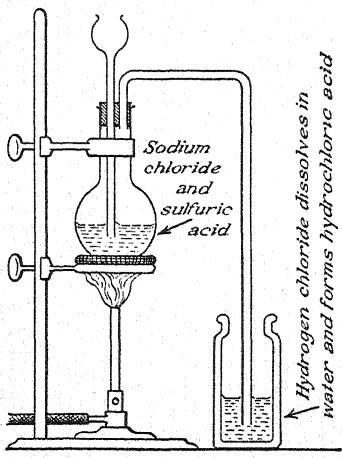
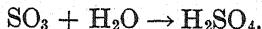
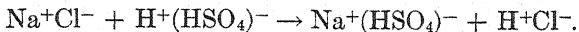


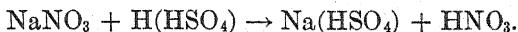
FIG. 105. — Laboratory preparation of hydrogen chloride and hydrochloric acid.

2. *Action of sulfuric acid upon salts.* If we examine the formula for hydrogen chloride,  $\text{HCl}$ , we see that it contains positive hydrogen and negative chlorine. Sulfuric acid contains positive hydrogen, and sodium chloride contains negative chlorine. Hence it seems possible to use the two to make hydrogen chloride. Experiment shows that the assumption is correct. (See Fig. 105.) Since sulfuric acid in a rather concentrated solution contains the  $(\text{HSO}_4)^-$  radical, which has a negative valence of 1, we may write the equation as follows:



The gas, hydrogen chloride, is driven off by the heat, and absorbed in pure water to form *hydrochloric acid*.

Nitric acid,  $\text{HNO}_3$ , is made in a similar manner. All nitrates contain the  $\text{NO}_3$  radical, but the cheapest nitrate is sodium nitrate,  $\text{NaNO}_3$ , a compound found extensively in Chile. If we heat this compound, sometimes called *Chile saltpeter*, with sulfuric acid, a reaction occurs which may be represented by the following equation:



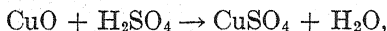
The nitric acid is vaporized by the heat used, but the temperature is not high enough to vaporize the sulfuric acid.

*Many acids may be prepared by heating with sulfuric acid a salt of the acid one wishes to prepare.* There are several reasons for using sulfuric acid: (1) *It supplies the hydrogen needed for the acids.* (2) *It is fairly stable.* (3) *It is the cheapest acid.* (4) *Its boiling point is higher than that of most acids.* If sulfuric acid is vaporized or decomposed at a temperature lower than that needed to vaporize other acids, the acid that is being prepared would be contaminated by either the sulfuric acid itself or by its decomposition products.

**154. General Physical Properties of Acids.** In physical appearance acids differ greatly. Some are colorless gases; others are colorless liquids. Citric, tartaric, boric, and oxalic acids are white, crystalline solids. Picric acid is a yellow, crystalline solid. Acids are water soluble.

**155. General Characteristics of Acids.** In their chemical behavior, acids have many properties or characteristics in common: (1) *They all contain hydrogen.* The student will recall that when Lavoisier named *oxygen* he thought that it was present in all acids. Oxygen is found in many acids, but it is the hydrogen in the acid that gives it its acid properties. (2) *Acids have a sour taste.* We know that lemons, grape fruit, and tomatoes are sour. The sour taste is so closely

associated with acids that we frequently use the term "acid taste." If the acids mentioned in Section 152 are to be tasted, they must first be made very dilute. (3) If we dip a piece of blue litmus paper into an acid solution, the blue will turn to red. Litmus is an organic dye extracted from lichens that grow along rocky seacoasts. Several other dyes serve as *indicators*; they change color in the presence of an acid. *We test for acids by means of indicators; acids turn blue litmus red.* (4) If we put together in the proper proportion an acid and a base, each destroys the properties of the other. This process is called *neutralization*. It is common to say *that acids neutralize bases.* (5) From the experiment on the preparation of hydrogen, we learned that *acids act on certain metals, liberating hydrogen and forming a salt.* (6) If we put some copper oxide in sulfuric acid, an interaction occurs. The equation,



is typical of the behavior of acids. *They act on the oxides of metals and form salts and water.*

**156. How Acids Are Named.** 1. *Binary compounds.* Acids that contain only two elements take their *root* from the negative element in them; they have the prefix *hydro-*, and the ending *-ic*. For example, HCl in water solution is called *hydro-chlor-ic* acid. The compound HBr dissolves in water; such a solution is called *hydro-brom-ic* acid. A water solution of the compound hydrogen sulfide,  $\text{H}_2\text{S}$ , is called *hydro-sulfur-ic* acid.

2. *Ternary acids contain both hydrogen and oxygen.* We may use the formulas for the various acids of chlorine to illustrate the method of naming such acids:

$\text{HClO}_4$ .....	<i>per-chlor-ic</i> acid.
$\text{HClO}_3$ .....	<i>chlor-ic</i> acid.
$\text{HClO}_2$ .....	<i>chlor-ous</i> acid.
$\text{HClO}$ .....	<i>hypo-chlor-ous</i> acid.



We note that they all contain hydrogen, which is implied in the name "acid." They all contain chlorine of varying valence; hence the root *chlor* is used in all of them. The *most common* oxygen acid is called *chlor-ic*. There is no prefix in this case. That acid which contains more oxygen than *chlor-ic* takes the same ending, but uses the prefix *per-* (thoroughly saturated with). The acid containing *one less* oxygen *atom* per molecule than the *-ic* acid takes the ending *-ous*; for example, chlorous acid,  $\text{HClO}_2$ . That acid which contains still less oxygen takes the ending *-ous*, and the prefix *hypo-* (from the Greek word meaning *under*).

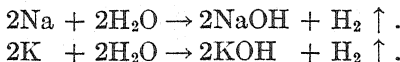
The student cannot be successful in getting the names of the different members of an acid series unless he memorizes the formula of the most common acid as a starting point. He has had the formula for sulfuric, nitric, and carbonic acids. The formula for phosphoric acid is  $\text{H}_3\text{PO}_4$ . A study of the following table shows that there are some irregularities and omissions, due to the fact that some elements do not form the full series of acids:

Acids	Formulas	Acids	Formulas	Acids	Formulas
sulfuric	$\text{H}_2\text{SO}_4$	nitric	$\text{HNO}_3$	bromic	$\text{HBrO}_3$
sulfurous	$\text{H}_2\text{SO}_3$	nitrous	$\text{HNO}_2$	—	—
<i>hypo</i> -sulfurous	$\text{H}_2\text{S}_2\text{O}_4$	<i>hypo</i> -nitrous	$\text{H}_2\text{N}_2\text{O}_2$	<i>hypo</i> -bromous	$\text{HBrO}$

## B. BASES

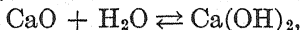
**157. The Most Common Bases.** As a rule, bases do not occur in nature. The student is doubtless familiar with such common bases as *aqua ammonia*,  $\text{NH}_4\text{OH}$ , common lye or sodium hydroxide,  $\text{NaOH}$ , lime water,  $\text{Ca}(\text{OH})_2$ , and milk of magnesia, which contains some magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ . Sodium hydroxide and potassium hydroxide are both white, deliquescent solids, very soluble in water. The soluble bases are called *alkalis*.

**158. How Bases Are Prepared.** 1. In the preparation of hydrogen, we learned that such active metals as sodium and potassium displace hydrogen from water and form bases. The equations follow:



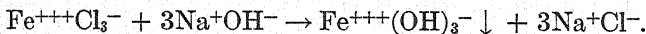
*One method of preparing bases consists in treating water with active metals.*

2. When a mason slakes quicklime,  $\text{CaO}$ , by adding water to it, he is preparing the base,  $\text{Ca(OH)}_2$ . The arrows show that the reaction,



is reversible. If we heat the base that is formed, we can *dehydrate* it and form the metallic oxide. This oxide is an example of a *basic anhydride*. *The oxide of a metal that will unite with water to form a base is called a basic anhydride.* This furnishes a second method of preparing bases.

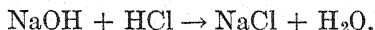
3. *Insoluble bases.* Suppose we add to a solution of ferric chloride a solution of some soluble base, such as sodium hydroxide. The reaction that occurs is shown by the equation:



The ferric hydroxide,  $\text{Fe(OH)}_3$ , is insoluble and it is thrown out of the solution as a reddish brown precipitate. Other insoluble bases may be prepared by this general method of *treating a soluble salt containing the metal with some soluble base.*

**159. The Characteristics of Soluble Bases.** (1) If we examine the formulas for all the bases we have studied, we find that *they contain some metal and one or more hydroxyl*

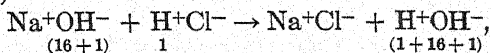
(OH) groups. (2) Most persons are familiar with the taste of milk of magnesia. *All soluble bases have a bitter taste.* (3) Indicators of various kinds are also sensitive to the action of bases. *Soluble bases turn red litmus blue.* The student must not confuse such change of color with that caused by acids. Neither must one get the idea that all indicators are turned blue by bases, for *phenol-phthalein* is turned red. Congo red is red in the presence of a base, but acids turn it blue. (4) Suppose we add 10 c.c. of a molar solution of sodium hydroxide to 10 c.c. of a molar solution of hydrochloric acid. The following equation shows us what happens:



The hydrogen, which is present in all acids, unites with the (OH) group, which is present in all bases, and forms water. The acid loses its properties and so does the base. Such a process is called *neutralization*. Incidentally, a *salt* is formed at the same time. (5) A solution of a strong base feels slippery when it is rubbed between the fingers. This is due to the fact that strong bases attack the flesh corrosively. They act upon the fatty portions and form soap. Because bases attack the flesh, they are said to be *caustic*. Sodium hydroxide used to be called *caustic soda*. An old name for potassium hydroxide is *caustic potash*.

**160. How Bases Are Named.** The method of naming bases is simplicity itself. We merely give the name of the metal, followed by the word *hydroxide*; for example, zinc hydroxide,  $\text{Zn}(\text{OH})_2$ . At one time hydroxides were called *hydrates*, and the name is still used to a slight extent.

★ **161. What Is Meant by a Normal Solution?** In Section 159, we learned that acids neutralize bases. In the equation,



we see that one mole of water (18 gm.) is obtained by the union of 1 gm. of hydrogen from one mole of  $\text{HCl}$ , with 17 gm. of  $(\text{OH})$  from one mole of the base,  $\text{NaOH}$ . Suppose we weigh out exactly 36.5 gm. of  $\text{HCl}$  and dissolve it in enough water to make exactly one liter. Such a standard solution contains exactly 1 gm. of replaceable (acid acting) hydrogen in 1000 c.c., or 1 liter. Chemists call such a solution a *normal solution* of hydrochloric acid, abbreviated *N-acid solution*. *A normal solution of any acid contains enough of that acid per liter of solution to yield exactly 1 gm. of replaceable hydrogen.* In order to make a normal nitric acid solution, one would need to dissolve 63 gm. of  $\text{HNO}_3$  ( $1 + 14 + 48$ ) in enough water to make one liter. To make a normal solution of sodium hydroxide, one must weigh out exactly 40 grams of the base to get the 17 grams of  $(\text{OH})$ , and dissolve it in enough water to make exactly 1000 c.c. *A normal solution of any base contains enough of that base per liter of solution to yield exactly 17 gm. of hydroxyl  $(\text{OH})$ .* With sodium hydroxide,  $\text{NaOH}$  ( $23 + 16 + 1$ ), we need 40 grams per liter. With potassium hydroxide,  $\text{KOH}$  ( $39 + 16 + 1$ ), we need 56 grams per liter.

If 1000 c.c. of a normal solution of any acid is added to 1000 c.c. of a normal solution of any base, we shall have complete neutralization. In other words, *normal acid solutions neutralize normal basic solutions, cubic centimeter for cubic centimeter.* It is possible to make up standard solutions that are 2, 3, or more times normal, or that are 0.1 N, 0.01 N, or any other fraction.

★ 162. **How the Chemist Uses Normal Solutions.** A man buys a sample of vinegar and he wishes to know what per cent of acetic acid,  $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ , it contains. He has a solution of a standard base that is just 0.1 normal in one burette, as shown in Fig. 106. The other burette he fills with vinegar to be tested. Next he draws off 10 c.c. of the vinegar in a flask, adds to it a few drops of a solution of phenol-phthalein,

which is colorless in acid solution, and then adds, slowly at first, and near the end drop by drop, the 0.1 N solution of the base until the last drop colors the solution red. The solution is now practically neutral. When he reads the base burette, he finds that it takes just 70 c.c. of 0.1 normal base to neutralize 10 c.c. of the acid of *unknown* normality. It is obvious, since it takes 7 times as much base as acid, that the acid must be *7 times as strong*. Therefore the vinegar contains 0.7-normal acetic acid. From the formula,  $\text{H}^+(\text{C}_2\text{H}_3\text{O}_2)^-$  we find that one mole, which is 60 gm., contains 1 gm. of replaceable hydrogen. The other hydrogen atoms are in the radical. Normal acetic acid contains 60 gm. of acid per liter; 0.7-normal acetic acid would contain 42 ( $0.7 \times 60$ ) gm. per liter, approximately 1000 gm. In 100 gm. there would be 4.2 gm. of acetic acid, or 4.2%. In a similar manner, the same standard base solution could be used to find the strength of any unknown acid. A standard acid solution may be used to find the strength of any unknown base.

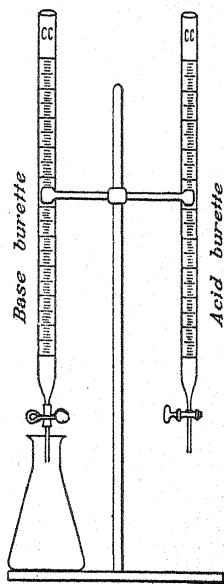


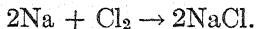
FIG. 106. — Burettes to be used for titration.

### C. SALTS

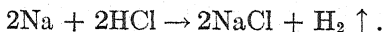
**163. Characteristics of Salts.** Because the properties of the thousands of salts known to chemists are so widely divergent, it is difficult to list any general properties. Most salts are to a greater or lesser degree soluble in water. The nitrates, which are salts of nitric acid, are all soluble. The majority of chlorides and sulfates are soluble. Salts are usually crystalline solids. Their color varies; the majority

of them are white, but cobalt salts are pink, copper salts are blue, nickel salts are green, manganese salts are pink, and the salts of *ferrous* iron are green.

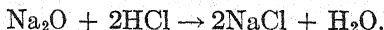
**164. How Salts Are Prepared.** There are several methods that are used in the preparation of salts. Let us study several methods of preparing common table salt, sodium chloride, NaCl, as typical of reactions that are quite general. One must wonder at the marvels of chemistry when he stops to think that sodium, a metal that displaces hydrogen from water, will burn in a jar of chlorine gas, a deadly poison, and form crystals of sodium chloride. (1) *By direct union of the elements* we prepare some salts.



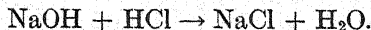
It is no less wonderful to learn that the same metal, sodium, will interact with hydrochloric acid, a poisonous corrosive liquid, and form nothing but sodium chloride and hydrogen. (2) *Salts are prepared by substitution of a metal for the hydrogen of an acid:*



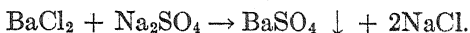
Is it not remarkable, too, that one can take the oxide of sodium, Na<sub>2</sub>O, and treat it with the same poisonous hydrochloric acid, and have formed nothing but sodium chloride and water? (3) *Salts are prepared by the interaction of the oxide of a metal with an acid.*



And what are we to say when the chemist adds sodium hydroxide, or caustic lye, to hydrochloric acid and then takes from his beaker nothing but sodium chloride and water? Is it strange that persons were mystified by the tricks of the alchemists? (4) *Many salts are prepared by neutralization.*



Sometimes it is possible to prepare *two* salts at one time by double decomposition. To accomplish the separation, however, one of them must be insoluble and the other soluble. If we add to a solution of barium chloride,  $\text{BaCl}_2$ , a solution of sodium sulfate,  $\text{Na}_2\text{SO}_4$ , metathesis occurs. The equation follows:



The barium sulfate is insoluble and may be removed by filtration. Then the sodium chloride can be recovered from the filtrate by evaporating the excess water. (5) *Metathesis is sometimes used to prepare two salts at the same time.* The student should remember that these reactions are typical of the methods of preparing salts. While all salts cannot be prepared by every one of the general methods given, yet the majority of them can be prepared by at least three of them.

**165. How Salts Are Named.** Since a salt is really the offspring of both a base and an acid, it seems fitting that it be named for both its parents. When we look at the formulas of the different salts that we have studied, we find that they are composed of the metal of a base and either an acid-forming element or an acid radical. If we were to neutralize each of the acids of the chlorine series listed in Section 156 with sodium hydroxide we would have a whole series of salts. Without bothering to write the sodium hydroxide factor, we may list the separate acids and the salts that would be formed from each acid.

ACIDS	SALTS
$\text{HClO}_4$ per-chlor-ic	$\text{NaClO}_4$ sodium per-chlor-ate
$\text{HClO}_3$ chlor-ic	$\text{NaClO}_3$ sodium chlor-ate
$\text{HClO}_2$ chlor-ous	$\text{NaClO}_2$ sodium chlor-ite
$\text{HClO}$ hypo-chlor-ous	$\text{NaClO}$ sodium hypo-chlor-ite
$\text{HCl}$ hydrogen chloride, or hydrochloric	$\text{NaCl}$ sodium chlor-ide



From the above table, we may formulate the following rule for naming salts: *Salts take the name of the metal of the base from which they were formed; they take the same root and prefix as the acid, but the acid ending "ic" is changed to "ate," and the ending "ous" is changed to "ite."* The salt from a binary acid ends in "*ide*."

### SUMMARY

Acids occur in green fruits, in citrous fruits, in tomatoes, and in soils. Nitric, hydrochloric, and sulfuric acids all find use in the industries. Some acids are gaseous; others, liquid; and still others, solid.

Acids are prepared: (1) By the union of the oxide of a non-metal, or *acid anhydride*, with water. (2) By treating a salt of the acid that is desired with sulfuric acid.

Sulfuric acid is used in preparing other acids for the following reasons: (1) It supplies the needed hydrogen. (2) It is cheap. (3) It is stable at moderate temperature. (4) It has a high boiling point. As a rule acids have the following characteristics: (1) They have a sour taste. (2) They contain hydrogen. (3) They turn blue litmus red. (4) They neutralize bases. (5) They act on metals forming a salt and setting free hydrogen. (6) They interact with oxides of metals and form a salt and water.

Binary acids are named by using the prefix *hydro-* and the ending *-ic* with the root of the negative element present in them.

The most common acid containing oxygen has the ending *-ic*. An acid in the same series containing less oxygen has the ending *-ous*. When an acid has still less oxygen than the *-ous* acid in the series, it takes the ending *-ous*, but uses the prefix *hypo-*. An acid having more oxygen than the *-ic* acid takes the *-ic* ending and uses the prefix *per-*.

All bases contain a metal and one or more *hydroxyl* (OH) groups. Bases are prepared: (1) By the action of active metals with water. (2) By the union of metallic oxides (basic anhydrides) with water. (3) Insoluble bases are prepared by treating a salt of the base required with some soluble base.

Soluble bases usually have the following characteristics:

(1) They contain hydroxyl (OH) groups. (2) They have a bitter taste. (3) They turn red litmus blue. (4) They neutralize acids. (5) They attack the flesh corrosively. With fats they form soaps.

Bases take the name of the metal from which they are formed and the word *hydroxide* is then added.

A *normal solution* of an acid contains one gram of replaceable hydrogen per liter. A normal solution of a base contains 17 grams of hydroxyl (OH) per liter. One cubic centimeter of any normal acid will exactly neutralize one cubic centimeter of any normal base. Normal solutions are known as *standard solutions*.

Salts may be prepared in several ways: (1) *Synthesis*. (2) *Neutralization*. (3) *Action of an acid on a metal*. (4) *Action of an acid with the oxide of a metal*. (5) *Double decomposition*.

Salts take the name of the metal of the base from which they are formed, use the same root and prefix as the acid, and change the acid ending *-ic* to *-ate*; the ending *-ous* to *-ite*.

## QUESTIONS

### GROUP A

1. Of what acid is  $\text{CO}_2$  the anhydride?  $\text{SO}_2$ ?  $\text{N}_2\text{O}_5$ ?  $\text{P}_2\text{O}_5$ ? Write the equation in each case for the forming of the acid. Use 3 molecules of water with the last one.

2. Take home several pieces of litmus paper and test several substances to see whether they are acidic or basic? Make lists of those that are acidic, neutral, and basic.

3. How would you test the soil of your lawn or garden to see whether it is too strongly acidic? If you find it strongly acidic, how would you remedy the condition?

4. What is the reason for adding a little lime water to the milk that is given to "bottle-fed" babies?

5. The human stomach digests protein in a solution slightly acidic due to the presence of hydrochloric acid. What does the doctor mean when he speaks of a case of "hyper-acidity"? What medicine might a doctor prescribe?

6. Which one of the bases mentioned in Section 157 would

you use to clean a greasy sink? To remove grease spots from a rug or from clothing? To neutralize acid stains on clothing?

7. What solution would you apply to an acid burn? To an alkali burn?

8. Write the name and formula of the salt formed by the action of each of the following acids on magnesium? (1) Hydrochloric; (2) sulfuric; (3) nitric; (4) acetic; (5) citric; (6) permanganic; (7) hypochlorous.

9. What products are formed by the action of each of the acids listed in No. 11 upon zinc oxide,  $\text{ZnO}$ ?

10. Make a list of foods that should not be stored in tin cans.

11. The following acids have the ending *-ic*: iodic,  $\text{HIO}_3$ ; bromic,  $\text{HBrO}_3$ . Write the names and formulas for as many other acids in the series as possible.

12. Is it correct to speak of sulfuric acid as hydrogen sulfate? Of nitric acid as hydrogen nitrate?

#### GROUP B

13. On milk of magnesia bottles one often sees the word "antacid." Without referring to a dictionary, give a scientific definition of the word.

14. If sodium hydroxide and potassium hydroxide were the same price per pound, which would you use as a base? Explain.

15. How many moles of sodium hydroxide are needed to neutralize one mole of hydrochloric acid? To neutralize one mole of sulfuric acid? To neutralize one mole of phosphoric acid?

16. What ending would you expect a salt to have if formed by the action of hydrochloric acid on a metal? What is the correct ending? Why?

17. What product would you expect to be formed by the reaction of a basic anhydride with an acid anhydride.

18. Phosphoric acid has the formula  $\text{H}_3\text{PO}_4$ . Write the formula for phosphorous acid. For hypo-phosphorous acid.

19. From the positions of silver and iron in the replacement series, Section 53, will a silver or a steel knife be stained more when used for cutting grapefruit?

20. What weight of sulfuric acid should be used in making up one liter of normal sulfuric acid?

21. What weight of barium hydroxide should be used in making up one liter of 0.01 normal barium hydroxide.

22. Silicic acid may have the formula  $\text{H}_4\text{SiO}_4$ . How many moles of sodium hydroxide are needed to neutralize one mole?

## PROBLEMS

## GROUP A

1. Balance and complete the following neutralization equations: (Remember that the products of such reactions are water and a salt.)



2. Balance and complete the following:



3. Give the correct names of all the salts formed in equations of Problems 1 and 2.

4. Write the equations for three methods of preparing the salt, potassium chloride, KCl.

5. Devise three methods for preparing calcium nitrate, and write the equations.

6. Classify the following compounds under one of the five headings; (1) acids, (2) bases, (3) salts, (4) acid anhydride, (5) basic anhydride:  $\text{Al(OH)}_3$ ;  $\text{P}_2\text{O}_5$ ;  $\text{H}_3\text{PO}_4$ ;  $\text{H}_2\text{CrO}_4$ ;  $\text{KMnO}_4$ ;  $\text{H}_2\text{F}_2$ ;  $\text{HClO}$ ;  $\text{Zn(OH)}_2$ ;  $\text{CaO}$ ;  $\text{K}_2\text{SO}_3$ ;  $\text{N}_2\text{O}_3$ ;  $\text{K}_2\text{O}$ ;  $\text{H}_3\text{PO}_3$ ;  $\text{NH}_4\text{OH}$ ;  $\text{SnCl}_2$ ;  $\text{AuCl}_3$ .

7. Give the chemical name for each of the compounds whose formulas are given in Problem 6.

8. How many grams of sodium hydroxide will be required to neutralize 85 grams of hydrogen chloride in water solution?

9. How many pounds of sulfuric acid will be needed to prepare 200 lb. of nitric acid? (See equation in Section 153.)

10. How many pounds of sodium nitrate will be needed to prepare 200 lb. of nitric acid?

## GROUP B

11. How many pounds of ferric hydroxide can be precipitated by the action of an excess of sodium hydroxide on 325 lb. of ferric chloride? (See equation in Section 158.)

12. From the equation given in Section 164, calculate the number of pounds of barium sulfate that can be prepared from 500 pounds of barium chloride, which is 95% pure.

13. How many c.c. of a 0.1 normal base will be needed to neutralize 25 c.c. of a 0.5 normal acid?

14. It is found that 34 c.c. of a 0.5 normal acid solution are needed to neutralize the ammonium hydroxide in 10 c.c. of a sample of aqua ammonia. Calculate: (1) the normality of the ammonium hydroxide; (2) the number of grams of ammonium hydroxide in one liter of the sample; (3) the percentage strength of the sample.

15. Calculate the per cent of iron in both  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ . Keeping in mind the fact that the ending 'ous' means 'full of,' explain why  $\text{FeO}$  is called ferrous oxide.

16. One hundred pounds of sodium hydroxide are added to 100 lb. of hydrochloric acid. How many pounds of sodium hydroxide, or, hydrochloric acid must be used to produce complete neutralization?

## CHAPTER 15

### THE ATMOSPHERE

#### Vocabulary

**Liquefy.** To change from either a gas or a solid to a liquid.

**Inert.** Not active chemically.

**Diluent.** A substance that dilutes another.

**Guano.** The excrement from sea-fowl.

**Weather.** (*Verb.*) To change solid rock into loose rock or soil.

**Hygrodeik.** An instrument used to read relative humidity directly.

**Caisson.** A closed compartment in which men can work underground or under water.

**Rectifier.** A device that changes alternating current to direct current.

#### A. THE AIR

**166. Introductory.** While the terms "air" and "atmosphere" have a slight difference in meaning, they are often used interchangeably. We have spoken of the importance of the air in our discussion of oxidation and combustion. We know that a part of this colorless, odorless, tasteless gas that we call "air" is oxygen. It cannot be composed wholly of oxygen, however, since pure oxygen is much more active. Then, too, one liter of air weighs 1.29 gm., considerably less than the weight of one liter of oxygen. Compared with the weight of one liter of water, 1000 gm., air seems very light and the expression "as light as air" is a common one. Although air is only about  $\frac{1}{7\frac{1}{3}}$  as heavy as water, yet a good-sized schoolroom contains several hundred pounds.

**167. Constituents of the Air.** In addition to oxygen, the air contains *nitrogen, argon, carbon dioxide, water vapor*, and several *rare gases*. Since other gases are naturally escaping into the air, *traces* of hydrogen sulfide,  $H_2S$ , sulfur dioxide,

SO<sub>2</sub>, ammonia, NH<sub>3</sub>, and other gases are present as impurities in certain localities. Ozone is formed in small quantity during thunderstorms. Particles of dust, bacteria, and smoke are always present in the air. The average per cent by volume of the more important constituents is as follows:

	Per cent
Oxygen.....	21
Nitrogen.....	78
Carbon dioxide.....	0.04
Argon.....	0.94
Water vapor, varies from a small fraction to as high as 2%.	

**168. How to Prove That Air Is a Mixture.** Several proofs may be given that air is a mixture and not a chemical compound:

1. The composition of the air varies slightly in different localities, and in the same locality at different times. We know that a compound always has a definite composition by weight.

2. If we mix the constituents in the same proportion in which they are found in air, there is no evidence of any chemical action, such as the evolution of heat and light.

3. If we take a sample of air that has been dissolved in water and analyze it, we find that it is about one third oxygen instead of the one fifth that is found by analysis of undissolved air. In other words, the oxygen of the air must be more soluble than the other constituents. A compound does not have its composition changed by dissolving it in water. *Therefore the air, which does, must be a mixture.*

4. When liquid air boils, the nitrogen boils off first, leaving the liquid oxygen. If air were a compound, all the constituents would boil off at the same time and in the same proportion.

Other proofs can be given to show that air is a mixture, but since its composition is not definite, since there is no evidence



of any absorption or release of energy when the constituents are brought together, since dissolved air has a different composition from undissolved air, and since the boiling point of air is not constant, we have abundant evidence that *air is a mixture*.

**169. What Is Liquid Air?** ~~We call water a liquid and~~ air a gas merely because they exure of oxygen and nitrogen. temperatures. Water become temperature is raised. Iron m: or it may even be changed into a sufficiently high temperature are sufficiently cooled, they li of gases, is cooled it becomes a liquid air mist was first prepar Cailletet and Pictet. In 1883 Poland prepared a considerable after that date, it began to be fessor Dewar in London.

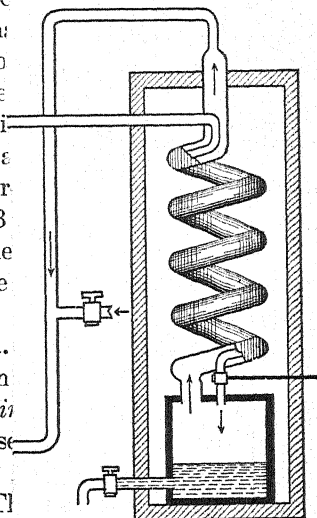
**170. How Air Is Liquefied.**

Faraday learned that certain cooling them and compressin them at the same time. He use

an apparatus like that shown Fig. 107 to liquefy chlorine. Th

chlorine was enclosed in a thick, walled, sealed tube. When or end of the tube was packed in: lower boiling point of the two, freezing mixture to cool the galy pure oxygen. At the same the other end of the tube was heated. The expansion of the gas in this end of the tube compressed the chlorine in the other end of the tube until some of it liquefied.

1. *The physical principle.* Those gases that Faraday could not liquefy by his method he called *fixed gases*. (See Fig. 108.) By the use of better methods of cooling, *all gases* have now been liquefied. If we open the valve of an inflated



Apparatus for liquefying air.

tire and hold one hand in the escaping gas, we notice a marked cooling effect. *Cooling always occurs when gases expand.* Heat is produced when gases are compressed. To liquefy gases, then, it is necessary to compress them, so they will expand *rapidly* when the pressure is released. The heat

Oxygen.....

Nitrogen.....

Carbon dioxide.....

Argon.....

Water vapor, varies from

of compression may be taken away by cold water surrounding the compressor. *Rapid* expansion may cool the remaining part of the gas to the temperature at which it will liquefy.

**168. How to Prove That** proofs may be given that air is a compound:

1. The composition of the localities, and in the same locality know that a compound always by weight.

2. If we mix the constituents which they are found in air by chemical action, such as the

3. If we take a sample of water and analyze it, we find it instead of the one fifth that dissolved air. In other words, more soluble than the other gases, not have its composition changed.

2. *The practice.* By the use of an apparatus like that shown in Fig. 109 the air is compressed by means of a pump. A pressure of from 3000 lb. to 4000 lb. per sq. in. may be used. The hot, compressed air then flows through a coiled pipe that is surrounded by cold water to absorb the heat. As the gas flows out through a *needle valve*, it expands rapidly and becomes cooled. This cooled gas then flows back through the outer of two concentric pipes and cools some of the gas in the inner pipe still more before it expands. When it expands, it is cooled to a still lower temperature. This process is repeated until the *critical temperature* is reached, a temperature to which a gas must be cooled before it can be liquefied by any pressure, no matter how great. This temperature is about  $-140^{\circ}\text{C}$ . for air. At such a temperature, with the high pressure

used, the gas begins to liquefy. Figure 110 shows a row of compressors for use in making liquid air at the Government plant at Muscle Shoals, Alabama.

**171. Properties of Liquid Air.** Liquid air resembles water in its appearance. Under ordinary atmospheric pressure, it boils at about  $-190^{\circ}\text{C}$ . Its boiling point is not constant, because it is a mixture of oxygen and nitrogen.

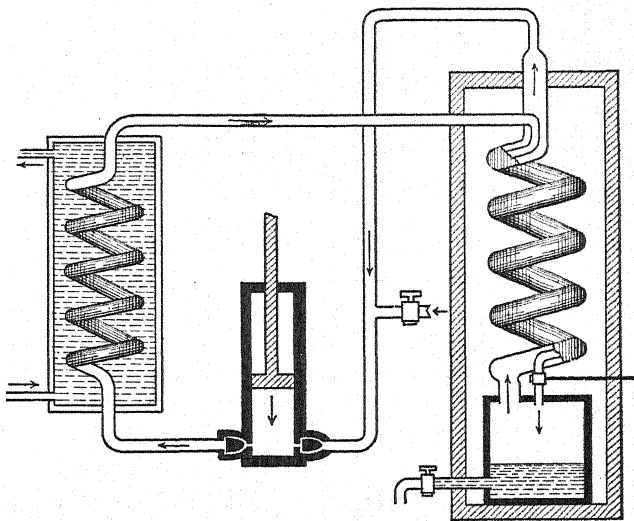


FIG. 109. — Linde's apparatus for liquefying air.

Because the nitrogen has the lower boiling point of the two, it boils away first, leaving nearly pure oxygen. At the same time the temperature rises to about  $-185^{\circ}\text{C}$ .

At such low temperatures, alcohol and carbon dioxide solidify. Mercury becomes frozen so hard that it can be used as a hammer to drive nails. A rubber ball immersed in liquid air, and then thrown on the floor, breaks as if it were made of glass. Tin becomes brittle, and lead elastic. If we put a piece of ice into a vessel of liquid air, the liquid air is

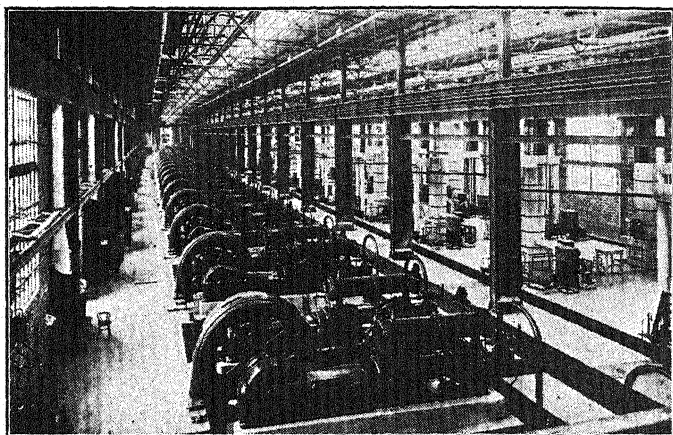


FIG. 110. — Compressors for making liquid air.

likely to boil over, because the ice is so hot in comparison. If one stops to think that boiling water is only 100 Centigrade degrees hotter than ice, and that *ice is about 190 Centigrade*

*degrees hotter than liquid air*, he may get a clearer idea of the extremely low temperature of this liquid.

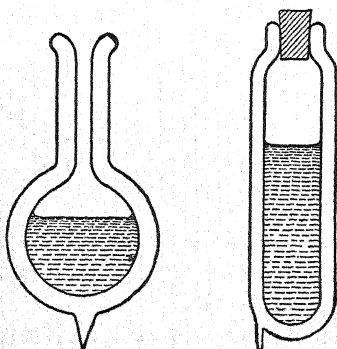


FIG. 111. — Dewar flask, cross-section.      FIG. 112. — Thermos bottle.

double-walled bottle like that shown in Fig. 111, for storing liquid air for a few hours. The space between the walls is a vacuum, so that heat from the outside will not be con-

**172. How Liquid Air Is Stored.** Since liquid air boils vigorously in an open vessel standing on a cake of ice, it is difficult to store it without great loss. Dewar

devised a flask,

ducted through the walls to the liquid. But heat rays, such as we receive from the sun, will penetrate both the glass and the vacuum. To prevent such rays from going through, the glass is silvered. The thermos bottle, Fig. 112, is constructed on the same principle.

**173. Uses for Liquid Air.** Liquid air is used to produce very low temperatures. We have already learned that it is a source of oxygen for commercial use. The nitrogen which boils off first finds use in filling electric bulbs and for making nitrogen compounds to be used either for fertilizer or in the manufacture of explosives. It is also a source of neon and argon.

## B. NITROGEN

**174. The Bulk of the Air Is Nitrogen.** Lavoisier's experiment, as described in Section 34, showed that about 80% of the air is inactive and will not combine with mercury. In 1772 nitrogen was discovered by Rutherford of Edinburgh. When Priestley put a live mouse in oxygen, it became very active; but when Rutherford put a live mouse in nitrogen, the mouse died. It was Lavoisier who named the gas *azote* (from the Greek words *a* and *zos* meaning "not life"). Because it is found in *niter*, or saltpeter, it was given the name "nitrogen."

**175. How Nitrogen Is Prepared.** 1. *From air.* We have already learned that the first gas that boils off from liquid air is nitrogen. That method is the one used in the commercial preparation of nitrogen. The nitrogen is not very pure when prepared by this method.

In the laboratory we may prepare nitrogen, contaminated with small percentages of other gases, by removing the oxygen from ordinary air. Several elements may be used for this purpose. If air is passed over hot copper gauze, the oxygen unites with the copper, and nitrogen is left. Other elements that can be used include mercury, carbon, or

phosphorus. If carbon is used, the nitrogen is contaminated with the carbon dioxide that is formed. We may put a little phosphorus in a crucible, float the crucible on water, ignite

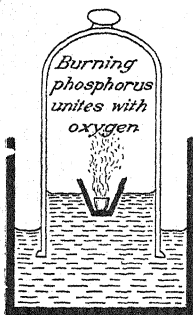


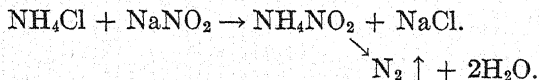
FIG. 113.— The gas left after the oxygen is removed is largely nitrogen.

the phosphorus, and immediately put a bell-glass over the crucible, as shown in Fig. 113. As the phosphorus unites with the oxygen of the air in the bell-glass, dense white clouds of fine particles of phosphorus pentoxide are formed. They dissolve in the water, which rises in the bell-glass to take the place of the oxygen that was removed. Nitrogen is left in the bell-glass. Incidentally, this method may be used to find the per cent of oxygen present in the air.

2. *From ammonium nitrite.* Pure nitrogen may be obtained by heating ammonium nitrite,  $\text{NH}_4\text{NO}_2$ . This compound decomposes directly into nitrogen and water.



In actual practice the nitrogen is prepared by heating a mixture of ammonium chloride and sodium nitrite, because ammonium nitrite may decompose explosively. These two compounds form the ammonium nitrite, which decomposes more slowly and yields the nitrogen. The equation that follows shows that the reaction probably proceeds in two steps, the second step being represented by the downward slanting arrow:



**176. Physical Properties of Nitrogen.** Nitrogen is a colorless, odorless, tasteless gas. It is slightly lighter than

air and slightly soluble in water. Nitrogen is not poisonous, but animals die in it from oxygen starvation.

**177. Chemical Behavior of Nitrogen.** Nitrogen is an *inert* gas. It neither burns nor supports combustion. During electrical storms, the lightning causes some nitrogen and oxygen to combine to make the compound *nitric oxide*, NO. In Norway use is made of this property of the electric spark in order to make nitric acid. The process is discussed in Section 199. By the use of a suitable catalyst nitrogen can be made to combine with hydrogen to form *ammonia*,  $\text{NH}_3$ . This process was devised by Haber, a German chemist. It is discussed in Section 193.

At high temperatures a few active metals, such as aluminum and magnesium, unite with nitrogen and form *nitrides*. Magnesium nitride,  $\text{Mg}_3\text{N}_2$ , interacts with water to form ammonia. This reaction serves as a *test for nitrogen*. To make the test for nitrogen, introduce the heated magnesium to form the nitride. Then when the water interacts with the nitride, the ammonia may be detected by its odor.

While compounds of nitrogen are usually formed with some difficulty, many of them are *unstable* and quite easily decomposed. Nearly all modern explosives are made of nitrogen compounds. They liberate large quantities of gas suddenly; hence their decomposition is very violent. Nitroglycerine, T. N. T., picric acid, and nitro-cellulose (smokeless powders), are examples of nitrogen compounds that explode with great violence.

**178. Nitrogen Is Very Useful.** Nitrogen in the air is a diluent. It makes combustion less rapid in air than in pure oxygen. It also gives bulk to the air, increasing its buoyant force and its pressure.

Nitrogen is used for filling electric bulbs; enormous quantities of nitrogen are also used in the manufacture of ammonia and nitric acid. Plants need nitrogen to make proteins, or albumin. They cannot use *free* nitrogen from the

air, however, but must obtain it from the *nitrogen compounds* in the soil. The *nitrogen cycle* in nature is a most important one. From the soil plants secure nitrogen compounds, water, and mineral matter, and with the carbon dioxide obtained from the air, they make proteins, or plant albumin. As decay occurs ammonia, nitrites, and nitrates are formed and re-

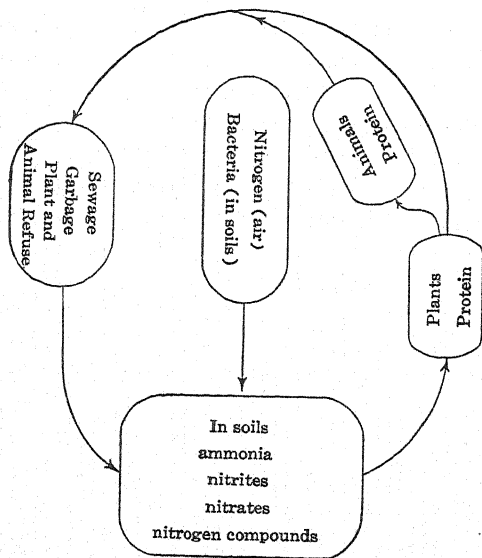


FIG. 114. — Nitrogen cycle in nature.

stored to the soil to be used for subsequent nutrition of plants. (See Fig. 114.)

Very often this natural cycle is interfered with, the plants being used for animal food and transported long distances; thus the nitrogen is removed from the soil and not returned by decay. The soil becomes impoverished and new crops cannot be grown unless some artificial fertilizer is used to take the place of the natural fertilizing process. The following are some of the most important methods used by farmers



for putting nitrogen back into soils that have lost their fertility:

1. *Refuse.* All plant and animal compounds contain nitrogen compounds upon which plants can feed. Ground bone, offal, and scrap from slaughter houses, refuse from fish

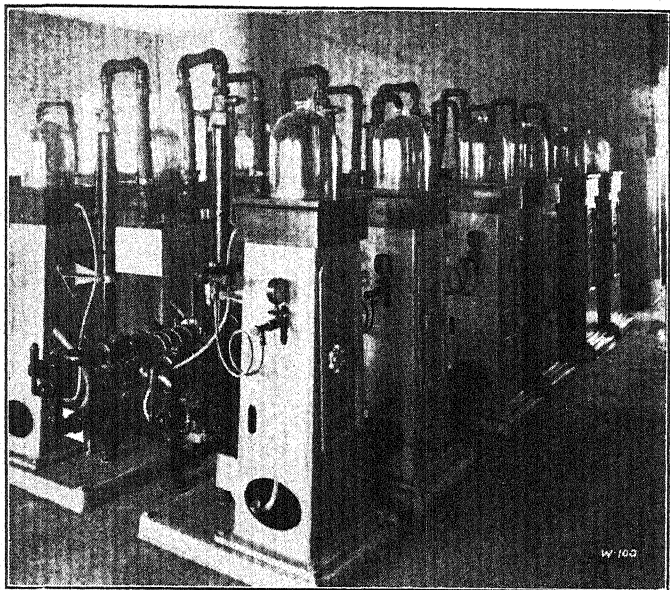
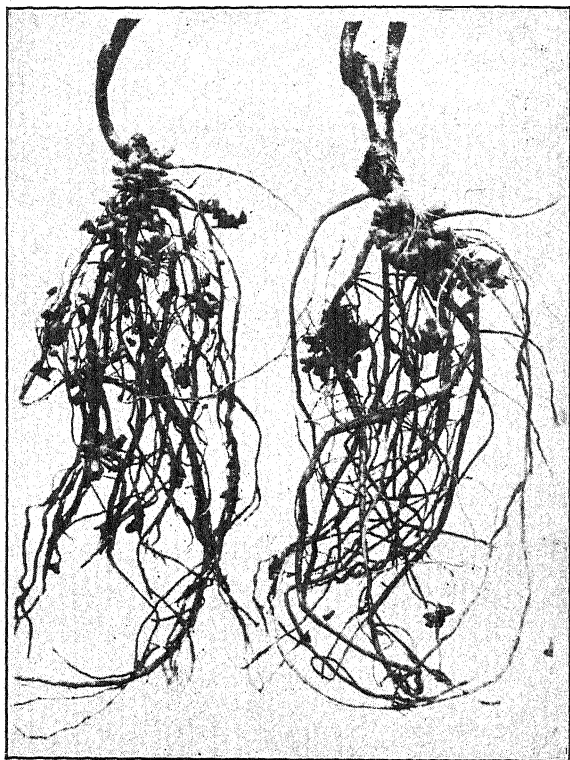


FIG. 115. — Chlorine cylinders for sewage purification.

canneries, garbage, sewage, guano, and barnyard manures are common materials used as fertilizers.

Both garbage and sewage are often wasted, and in many cities large sums of money are paid for the disposal of these products. In some cities both are dumped into rivers, lakes, or the ocean. Garbage is often incinerated. Some progressive cities have garbage reduction plants. Fats and grease are recovered from the garbage by treatment with steam or a petroleum solvent, and used for making soap. The solvent is

recovered and used over and over again. The nitrogen-bearing residues which are insoluble are dried and sold to fertilizer manufacturers under the name of *tankage*. Some



*J. Russell Smith, Commerce and Industry, by permission*

FIG. 116.—Nodules containing bacteria that take nitrogen from the air.

cities sterilize their sewage by aëration or the use of chemicals and then sell it for use as a fertilizer. Figure 115 shows cylinders of chlorine that are being used to purify sewage by destroying bacteria.

2. *Crop rotation.* We have seen that the continued planting of a single crop that is removed from the farm year after year leaves the soil impoverished. There are certain crops, however, that the farmer can grow which put nitrogen compounds into the soil. Peas, alfalfa, beans, and clover all have small *nodules* on their roots. (See Fig. 116.) Bacteria that are friends to man grow in these nodules. These bacteria in an alkaline soil can take *free* nitrogen from the air and convert it into compounds that plants can use. For breathing we must have *free* oxygen and we would die in water which is 88% oxygen, but in combination. Plants live in air that is 78% *free* nitrogen, but they cannot take it from the air; they are wholly dependent upon nitrogen *compounds* which can be taken in through the roots when dissolved in the soil water. By planting a crop of clover, cow peas, or soy beans every four or five years, the farmer has a fodder crop and at the same time he is putting nitrogen into his soil through the friendly aid of these bacteria. Some Experiment Stations grow these bacteria and supply them to farmers for inoculating seeds before they are put into the ground.

3. *Nitrate beds.* In South America, principally in Chile, extensive beds of sodium nitrate have been discovered in the desert regions. These beds have for a number of years been an important source of sodium nitrate for use as a fertilizer or for making explosives.

4. *Nitrogen compounds made artificially.* Taking free nitrogen from the air and converting it into compounds is commonly known as *nitrogen fixation*, or *nitrification*. Several processes are now in use. The processes of making nitrogen compounds are discussed in later chapters. In 1903, Chile supplied as sodium nitrate about 63% of the combined nitrogen used, a total of 435,000 tons. In the year 1933, more than 120 plants, operating in 19 countries, made 1,700,000 tons of 'artificial' nitrogen, working at 50% capacity. Chile supplied one-tenth that amount.

## C. CARBON DIOXIDE

**179. Introductory.** It was Joseph Black, a Scotch chemist, who first noticed that carbon dioxide is different from the other gases found in air, and from air itself. He called the gas "fixed air." Since we know that animals exhale carbon dioxide to the air, and that one of the products of ordinary combustion is carbon dioxide, common sense tells us that there must be carbon dioxide present in the air at all times.

**180. Factors that Increase the Amount of Carbon Dioxide in the Air.** The amount of carbon dioxide in outdoor air is about 4 parts in 10,000, and the percentage varies only a little. Over some cities, it may reach as much as 7 parts in 10,000. There are three important factors that are reducing the per cent of oxygen in the air and *increasing the per cent* of carbon dioxide: (1) All fuels contain carbon. When carbon burns in a sufficient supply of air, carbon dioxide is formed. Every ton of carbon that is burned takes  $2\frac{2}{3}$  tons of oxygen from the air, and gives off  $3\frac{2}{3}$  tons of carbon dioxide to it. (2) Practically all animal foods contain carbon. The slow oxidation that occurs during the respiration of animals forms carbon dioxide, which is exhaled to the air. Hence, animals during breathing are reducing the amount of oxygen and increasing the amount of carbon dioxide. (3) When vegetable and animal matter decay, one of the products formed is carbon dioxide. This gas finds its way to the air, and helps to increase the percentage already present.

**181. Factors that Decrease the Amount of Carbon Dioxide in the Air.** We have learned that the per cent of carbon dioxide in the air remains nearly constant, despite the fact that there are three factors that are constantly increasing the amount. It follows that there must be some important factors at work reducing the amount. There are two important ones: (1) Some of the carbon dioxide dis-

solves in water, and this solution acts like a weak acid. It attacks the rocks of the earth's crust as they weather, or disintegrate, and carbonates are formed. Thus the carbon dioxide becomes a part of soils and rocks. (2) All plants that have green coloring matter in their leaves or other tissues take in carbon dioxide and give off oxygen during the process of making starch. Figure 117 shows how a leaf acts as a starch factory. The raw materials include carbon dioxide

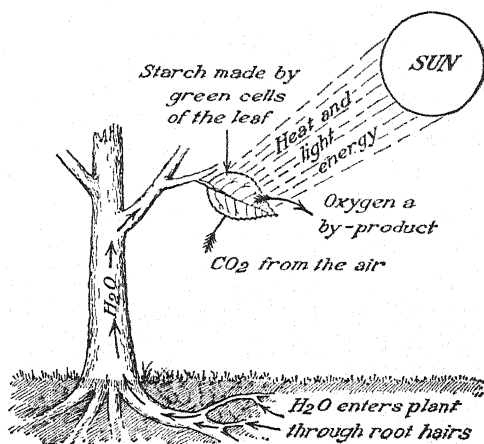


FIG. 117. — A green leaf is a factory fitted to manufacture starch.

from the air, and water that enters through the roots. The energy is the sunlight. Hence this process is called *photosynthesis* (from the Greek words *phos*, meaning "light" and *sunthesis*, meaning "putting together"). The green coloring matter in the leaves serves as the machinery, and the waste material is oxygen, which is given back to the air.

**182. The Oxygen-Carbon Dioxide Cycle.** We have had mentioned three ways in which the amount of carbon dioxide in the air is being increased constantly. We have also studied two ways in which the amount is being reduced.

The part played by plants and animals is shown in the diagram of Fig. 118. The plants make our foods for us, and they take carbon dioxide from the air and give oxygen back to the air. Animals eat the foods that plants manufacture, take oxygen from the air, and give back to the air the carbon dioxide which is needed by plants in their work of making starch. Hence, animals and plants are *mutually dependent*. The *oxygen-carbon dioxide cycle* may be briefly stated:

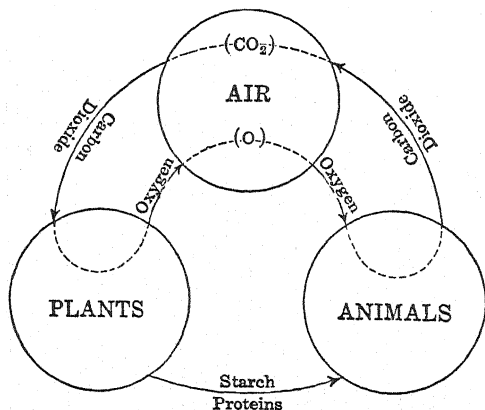
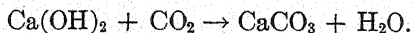


FIG. 118. — Carbon dioxide cycle.

*Animals inhale oxygen and exhale carbon dioxide; plants absorb carbon dioxide during photosynthesis and give out oxygen.* Plants do breathe the same as animals, but in sunlight the amount of carbon dioxide they use is much greater than the amount they exhale.

**183. How to Test for Carbon Dioxide.** If we blow our breath through lime water, a white precipitate of calcium carbonate,  $CaCO_3$ , is formed. This milky white precipitate formed when a gas is bubbled through lime water serves as a test for carbon dioxide. The chemical equation follows:



## D. WATER VAPOR

184. Water Vapor in the Air. Deliquescent substances become wet when exposed to the air. A glass of ice water standing in a warm room soon becomes covered with drops of water. These tests, as well as the fact that rain falls occasionally, show that the air contains water vapor.

The *amount of water vapor the air can hold is its capacity*. It is usually expressed in grains per cubic foot. The capacity increases as the temperature rises. *The amount of water vapor the air does hold at a given time is called its absolute humidity*. Absolute humidity is expressed in grains per cubic foot. The absolute humidity of outdoor air depends upon several factors, but chiefly upon proximity to a large body of water from which evaporation may occur.

*The relative humidity equals*  $\frac{\text{absolute humidity}}{\text{capacity}}$ . Raising the

temperature *decreases* the relative humidity and the air feels drier since the capacity is increased by a rise in temperature. Lowering the temperature lowers the capacity and *increases* the relative humidity, making the air feel damp. When the relative humidity become 100%, the *dew-point* is reached. A further cooling of the air then results in precipitation of some of the moisture as rain, snow, etc.

A high relative humidity makes the heat oppressive in summer and the cold seem more severe in winter. We say the air is "heavy." In reality it is "light," since 1 liter of water vapor at standard temperature and pressure weighs only 0.81 gm. When the relative humidity is too low, the perspiration evaporates rapidly and the skin feels dry; when the relative humidity is very high, the perspiration does not evaporate and the skin is clammy and sticky. We are most comfortable when the relative humidity is from 40% to 60%.

**185. What Is Meant by Air-conditioning?** The average adult eats about a ton of food every year, but in the same period of time he breathes over six tons of air. Much money and effort are spent in keeping his food clean and wholesome, but relatively little attention is given to the proper conditioning of his air.

At one time it was believed that we must ventilate our living and sleeping rooms because the increase in the per cent of carbon dioxide made the air unfit to breathe, but

research work has shown that it is not the carbon dioxide that causes discomfort in poorly ventilated rooms. The engineer learned that the humidity of the air in a factory has much to do with the spinning of cotton or rayon. In turning his attention to air-conditioning for man, he finds that four things are necessary for man's health and comfort: 1. The air must be warmed in winter and cooled in summer. Man can adapt himself

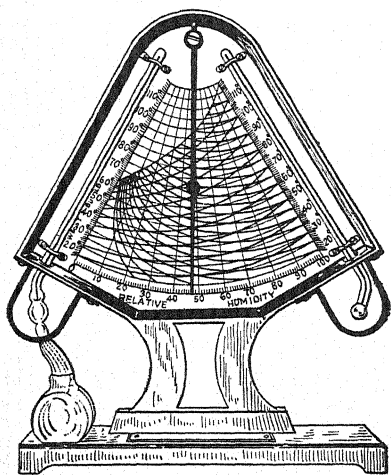
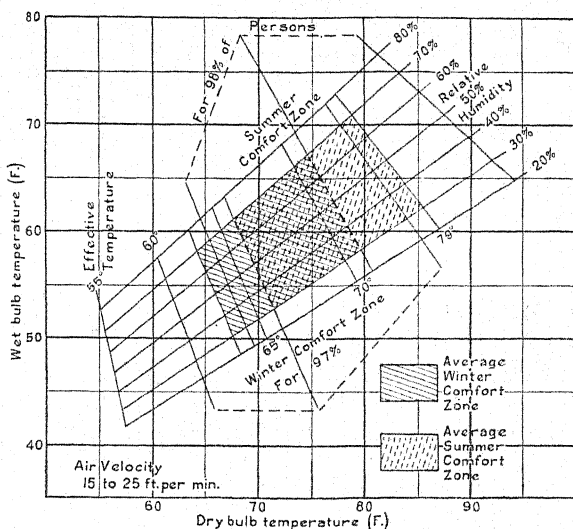


FIG. 119. — The hygrodeik measures dew point, absolute and relative humidity.

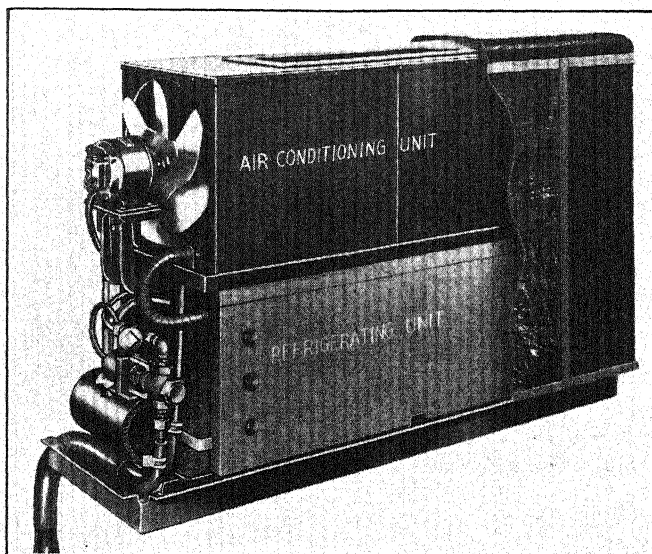
to extreme temperatures, but he does his best work when the temperature range is from 63° F. to 75° F. 2. The relative humidity should not be less than 30% nor more than 70%, preferably between 40% and 60%. One frequently hears an uncomfortable person say: "It is not the heat, but the humidity." (See Fig. 119a.) 3. The air should be filtered to remove the dust particles and bacteria that are always present in the air. The accumulation of dust par-





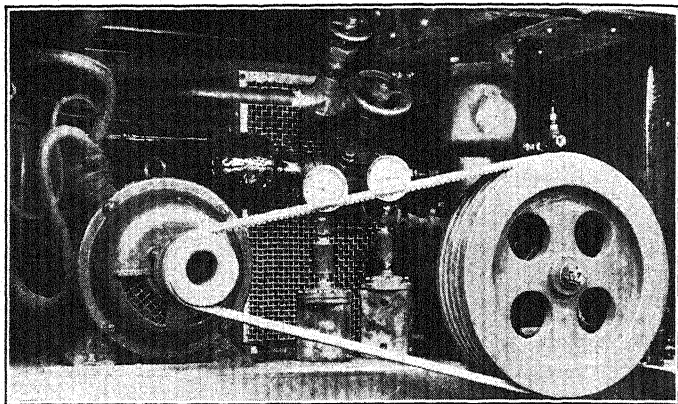
*Courtesy of Westinghouse Electric and Manufacturing Co.*

FIG. 119a. A chart which shows the conditions under which a person is comfortable.



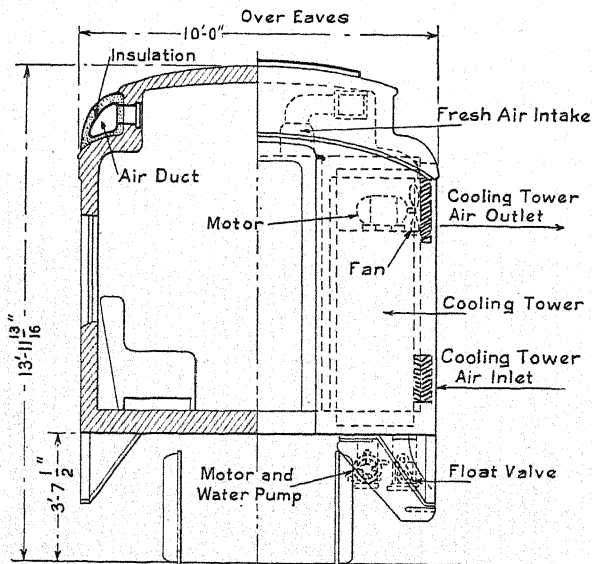
*Courtesy Westinghouse Electric and Manufacturing Co.*

A view showing the different parts of an air-conditioning unit.



*Courtesy of Baltimore and Ohio Railroad*

Compressor installed beneath car is driven by flexible belt. It is used to compress the refrigerant.



This chart shows the manner in which the air is circulated through a passenger car of this air-conditioned train.

tion of the finely divided tungsten which would condense upon it. The argon is too lazy to unite chemically with the tungsten, and it gets in the way of the tungsten particles that are trying to escape from the filament. Argon also finds use for filling the bulbs used in making tungar rectifiers for charging storage batteries.

**188. Discovery and Preparation of Helium.** It is interesting to learn that an element may be found in the sun's atmosphere before anyone finds it on the earth. But by the use of the spectroscope, in 1868 Sir Norman Lockyer dis-

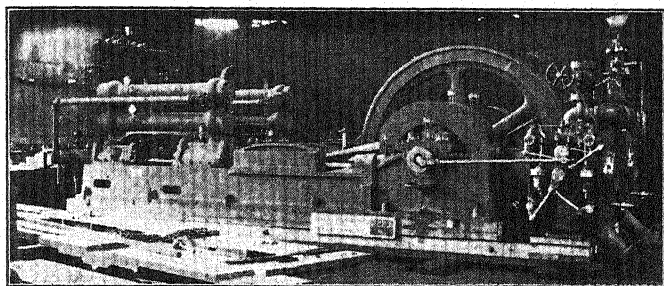


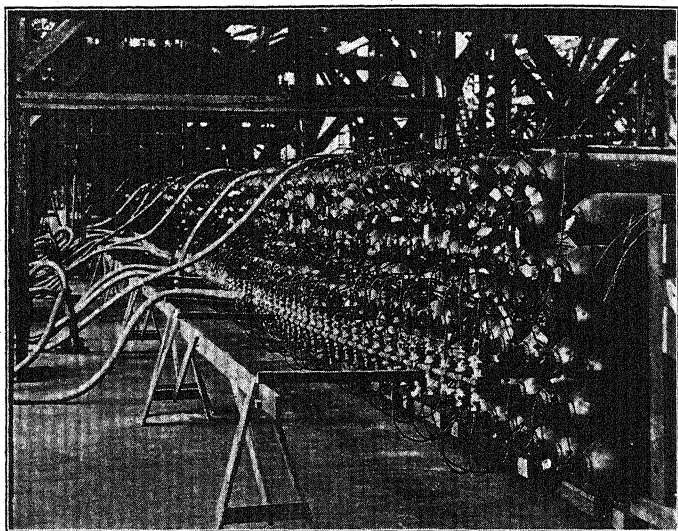
FIG. 122. — Compressor used at Fort Worth, Texas, for liquefying helium.

covered helium in the sun's atmosphere. The gas was named helium, from the Greek word *helios*, which means "sun." It was 27 years later that it was found by Sir William Ramsay to be one of the constituents of our atmosphere. (See Fig. 121.)

Prior to the World War, helium sold at the rate of about \$1700 a quart. When its importance for military purposes was realized, search was made for a more abundant supply. In some of the natural gas wells of Kansas, Oklahoma, and Texas, the gas was found to contain 2% or more of helium. Figure 122 shows a compressor used for obtaining helium from natural gas. By the use of such compressors, everything

except the helium is liquefied by compression and cooling. In this manner helium may be separated from the other constituents of natural gas at a cost of less than 2¢ per cu. ft.

**189. Properties and Uses of Helium.** Although helium is about twice as heavy as hydrogen, it is more than 92% as efficient as a buoyant agent. The student must remember



*Courtesy of U.S. Navy*

FIG. 123. — Steel cylinders used for storing helium.

that the so-called buoyancy of a gas is equal to the difference in weight between a given volume of air and the same volume of the gas. Helium is non-flammable. Since it cannot be kindled by incendiary bullets, or by any other means, it is almost an ideal gas for use in dirigibles. The United States appears to have almost a monopoly on the supply of helium. When the *Los Angeles* was brought to the United States from Germany, the hydrogen was removed from its gas bags, and they were filled with helium. Figure 123 shows steel

cylinders used for storing helium, and Fig. 124 shows a huge cylinder used for its transportation.

Helium forms no compounds. It is the most difficult gas to liquefy. Its boiling point is  $-268.5^{\circ}\text{C}.$ , as determined by Kamerlingh Onnes who first liquefied helium in 1908. By evaporating frozen helium, de Haas obtained a tempera-



*Courtesy of U. S. Navy*

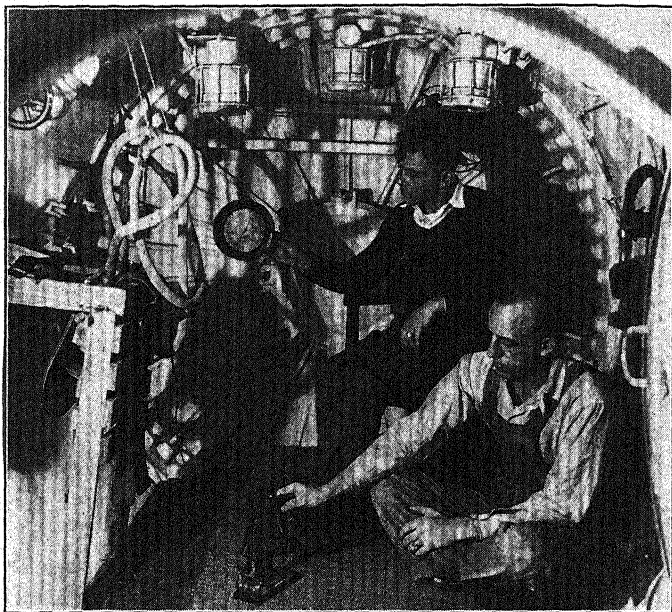
FIG. 124. — Helium is transported from the gas-wells to Lakehurst, New Jersey, in such cylinders.

ture within 0.003 of a Centigrade degree of Absolute zero. The freezing point of helium is  $-272.2^{\circ}\text{C}.$

Divers and men who work in caissons for constructing tunnels or under-water piers are forced to work in an atmosphere of compressed air. Under such conditions, nitrogen dissolves in the blood and even in the spinal cord. If the high pressure is released too quickly, bubbles of nitrogen are formed in the blood and tissues of the body. This causes "caisson disease," or "the bends," and the men may collapse or even die from it. To prevent such a disease, the men are kept in decompression chambers for some time, and the pressure is there reduced gradually. Now helium and oxygen

are being used in such chambers, because helium is less soluble than nitrogen in the blood and tissues of the body, and it is released more rapidly when decompression occurs. The workmen are thus brought back to normal pressure more quickly and more safely. (See Fig. 125.)

**190. The Rare Gases.** By fractional distillation of the gases remaining after the removal of oxygen, nitrogen,



*Courtesy of U.S. Bureau of Mines*

FIG. 125. — Note the apparatus for use in the decompression chamber in which divers are placed. An oxygen-helium mixture of gases is used in the chamber. The valves can be controlled from the inside or the outside.

water vapor, and carbon dioxide from the air, Ramsay discovered three other gases present with the argon that was left. These gases were named *neon* (from the Greek word *neos*, "new"), *krypton* (from the Greek *kruptos*, "hidden")



and *xenon* (from the Greek *xenos*, "strange"). Neon is present to the extent of about 1 part in 20,000 of air, but there is only about 1 part of xenon in 20,000,000 parts of air. All of these gases are inert and form no compounds.

**191. The Uses of Neon.** Everyone is familiar with bent glass neon tubes that are so much used for advertising pur-

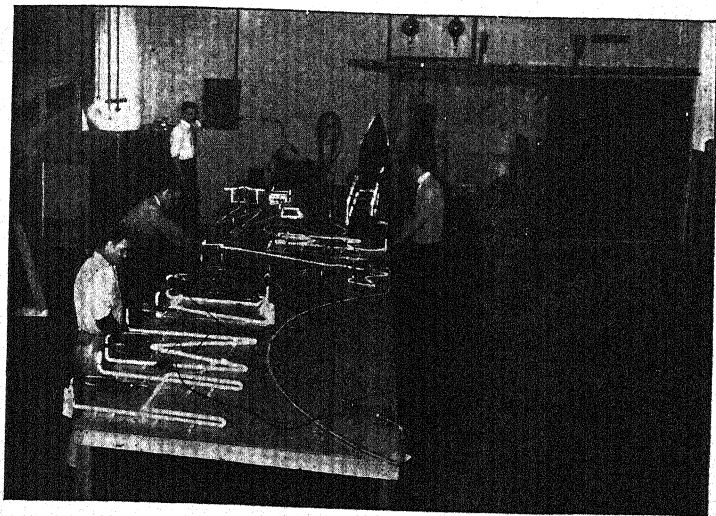


FIG. 126. — Making neon tubes for advertising signs.

poses. In the ends of such tubes, electrodes are sealed, and the tubes are filled with neon gas. When the current is turned on, the whole tube glows as the neon vapor conducts the current through the tube. The amount of current used is so small that the cost of operating such advertising signs is small. The addition of a little mercury vapor to the neon in the tube imparts a blue color. Other color effects may be obtained, either by the use of colored glass, or by the use of traces of other gases. (See Fig. 126.)

The reddish-orange color of the neon light seems to pene-

trate fog better than other light. Hence neon lamps are being used as beacons for aviators.

In a tungsten lamp it takes a fraction of a second for the filament to begin to glow, and a fraction of a second for it to stop glowing. The light from a neon lamp does not lag in this manner, but it is on instantly and off instantly. This behavior makes it suitable for use as a light in television apparatus. Any fluctuations in the light at the transmitting end of the apparatus produce instantly the same fluctuations in the neon lamp at the receiving end.

### SUMMARY

Air has weight and it exerts pressure. Nearly 99% of the air is made up of *nitrogen* and *oxygen*. Argon occupies about 0.9 of 1%. There are small quantities of carbon dioxide, water vapor, argon, neon, krypton, and xenon.

*Air is a mixture:* its proportion varies slightly; it dissolves as a mixture; it boils as a mixture.

By compression and cooling, air may be liquefied. Liquid air has a very low temperature. It is used as a commercial source of nitrogen, oxygen, argon, and neon.

*Nitrogen* may be obtained from the air by removing the oxygen with some chemical, such as phosphorus or copper. Pure nitrogen is prepared by heating a mixture of ammonium chloride and sodium nitrite.

*Nitrogen* is colorless, odorless, and tasteless; it is non-poisonous, but animals die in it from suffocation. Nitrogen is slightly soluble in water, and slightly lighter than air.

*Nitrogen* neither burns nor supports combustion. It is difficult to make it combine with other elements, and its compounds are not very stable. Under proper conditions, nitrogen may be made to combine with hydrogen to form ammonia; with oxygen to form nitric oxide; or with magnesium or certain other metals to form nitrides.

*To test for free nitrogen*, we heat the gas with magnesium. If nitrogen is present, it will unite with the magnesium and form



magnesium nitride which in turn will form ammonia with water. The ammonia is detected by its odor.

*Nitrogen compounds* are needed by plants to form proteins. Such compounds are obtained from decaying plant and animal tissues. They occur to some extent in nature. They are made by some bacteria. Man has learned to take nitrogen out of the air and make it into compounds for the use of plants. The process is called *nitrification*, or *nitrogen-fixation*.

*Plants take in carbon dioxide and give out oxygen; animals inhale oxygen and exhale carbon dioxide.* This exchange forms the *oxygen-carbon dioxide cycle*.

The fact that carbon dioxide will interact with lime water and form a milky, white precipitate serves as a *test for carbon dioxide*.

*Humidity* refers to the presence of water vapor in the air. The amount of water vapor air *can* hold at a given temperature is its *capacity*. The amount of water vapor the air *actually does* hold is its *absolute humidity*. The *relative humidity* is the ratio of the absolute humidity to the capacity. It tells us how many per cent full the air is of moisture.

*Argon* is a lazy, inactive element found in the air. It finds use in gas-filled electric bulbs.

*Neon, krypton, and xenon* are rare gases found in the air. Neon finds some use in advertising signs, and in lights for airport beacons and for television apparatus.

## QUESTIONS

### GROUP A

1. How would you prove that air is a mixture?
2. Why does liquid air boil so vigorously when poured on a cake of ice?
3. Why does liquid air become blue when it stands for some time? Explain why a piece of burning charcoal will continue to burn vigorously if held under such liquid.
4. Why do the properties of nitrogen prepared from ammonium nitrite differ from those of the nitrogen obtained by removal of the oxygen from the air?

5. What is meant by nitrification, or nitrogen fixation? Explain why the process is so important.

6. How can the oxygen be removed from ordinary air? How would you remove the nitrogen from air?

7. What is the test for nitrogen in the uncombined state?

8. How could you obtain air that is free from carbon dioxide? From water vapor?

9. Given one bottle of each of the following gases: oxygen, nitrogen, hydrogen, and carbon dioxide. How would you make chemical tests to identify each one?

10. What is meant by crop rotation? Of what value is it to a farmer?

11. Explain fully what is meant by the oxygen-carbon dioxide cycle.

12. Explain fully what is meant by the nitrogen cycle.

13. How is hydrogen superior to helium for use in balloons? In what ways is helium superior to hydrogen?

14. What is meant by air-conditioning?

#### GROUP B

15. How would plants and animals be affected if the per cent of oxygen in the air were increased?

16. Would it be a good idea to stopper a thermos bottle or a Dewar flask containing liquid air? Explain.

17. Can it ever rain while the air is being warmed? Is compression or expansion of air more likely to produce rain? Explain.

18. Why are traces of nitrogen compounds found in the air after thunderstorms?

19. More fuel is burned in winter, and plants are not then making starch. Does the per cent of carbon dioxide increase at that time? If not, explain why not.

20. How is helium helpful in the construction of such tunnels as the Holland Tunnel under the Hudson River?

21. In hospitals, the nurses remove the flowers and plants from the sick rooms at night. Is there a good reason for such practice?

22. In the preparation of nitrogen from the air, why is carbon

not very satisfactory as an element for removing the oxygen? Name an element that is more satisfactory.

23. The following substances are exposed to air: phosphorus, anhydrous calcium chloride, hot magnesium, and lime water. What substance or substances does each one remove from the air?

24. What is meant by the term "critical temperature" as applied to a gas?

25. What is meant by the term "critical pressure" as applied to gases?

## PROBLEMS

### GROUP A

1. How many grams of sodium chloride are prepared by the action of an excess of sodium nitrite on 107 gm. of ammonium chloride?

2. How many pounds of calcium hydroxide are needed to absorb 132 lb. of carbon dioxide? (See equation, page 238.)

3. How many pounds of calcium carbonate are formed in the reaction of Problem 2?

### GROUP B

4. How many liters of nitrogen are prepared in the reaction of Problem 1?

5. How many liters of carbon dioxide at S. T. P. are needed to unite with 185 gm. of calcium hydroxide?

## SUPPLEMENTARY PROJECTS

Prepare a report on one of the following topics:

1. The story of the discovery of the rare gases of the atmosphere.

Reference: DARROW, FLOYD L., *The Story of Chemistry*, pages 43, 47, 208-210. Bobbs-Merrill.

2. The work of Onnes dealing with low temperatures.

Reference: *Scientific American*, Oct., '23; Aug., '23; Feb., '27.

3. The spectroscope and its use in chemistry.

References: DARROW, FLOYD L., *The Story of Chemistry*. Bobbs-Merrill.

*Encyclopedia Britannica*. (See Index.)

## CHAPTER 16

### AMMONIA AND AMMONIUM COMPOUNDS

#### Vocabulary

**Detergent.** A substance used as a cleansing agent.

**Heat of vaporization.** The number of heat units needed to change 1 gm. of a liquid at its boiling point into vapor at the same temperature.

**Brine.** A solution of a salt in water, usually of sodium chloride or calcium chloride.

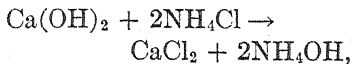
**Autoclave.** A strong, gas-tight vessel, used for heating substances under pressure.

**192. Introductory.** A solution of ammonia gas in water is known as *household ammonia*. It is the pungent gas that arises from such a solution that is known to chemists as *ammonia*. It has the formula  $\text{NH}_3$ . Traces of ammonia are found in the air, since this gas is formed by the decay of plant and animal matter. As it dissolves in the rain water it finds its way into the soil, where it is taken up by the roots of plants; it is also formed by the decay of organic matter in the presence of bacteria that cause putrefaction. The odor of ammonia may be noticed in the vicinity of stables where farm animals are housed.

**193. How Ammonia Is Prepared.** Ammonia can always be prepared by decomposing ammonium compounds. It may be obtained from coal and from shale rock, or it may be made synthetically by the union of nitrogen and hydrogen.

1. *Laboratory preparation.* If we put a mixture of slaked lime and some ammonium compound in the palm of the hand and rub the mixture with a finger, the odor of ammonia

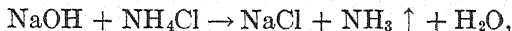
gas may be detected. When a mixture of slaked lime,  $\text{Ca}(\text{OH})_2$ , is heated with ammonium chloride,  $\text{NH}_4\text{Cl}$ , in a test tube arranged like that shown in Fig. 127, ammonia gas is driven off by the heat. This gas is too soluble to be collected by water displacement. It is collected by air displacement. In the equation,



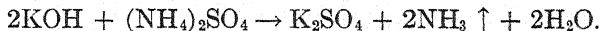
the ammonium group,  $\text{NH}_4$ , acts as a positive radical and takes the place of calcium by substitution. But the compound  $\text{NH}_4\text{OH}$  is unstable, and the heat of the reaction breaks it up into ammonia and water.



Any strong base may be used instead of the calcium hydroxide, and any ammonium salt may be substituted for the ammonium chloride. For example,



or



2. *Commercial sources.* (a) *From coal.* At one time ammonia was prepared by distilling hoofs and horns; hence the old name "spirits of hartshorn." Now one of the important commercial sources of ammonia is soft coal. When coal is heated in retorts to prepare illuminating gas, ammonia is given off as a by-product. The ammonia dissolves in the water used to wash the gas, and the solution is neutral-

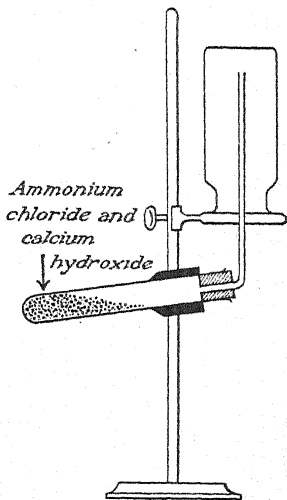
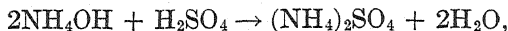


FIG. 127. — Laboratory apparatus for use in preparing ammonia.

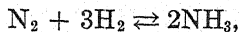
ized with sulfuric or hydrochloric acid. When sulfuric acid is used,



ammonium sulfate is formed. This salt is then decomposed with slaked lime, and the ammonia is dissolved in pure water. (See equation under laboratory preparation.) Such a solution forms the *aqua ammonia* of commerce.

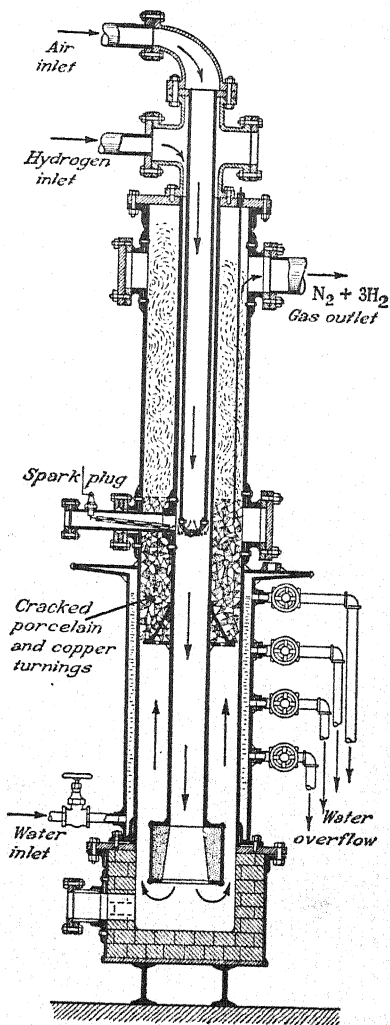
(b) *From oil-bearing shale rock.* Some of the shale rocks in Colorado, Utah, and Wyoming contain petroleum that can be obtained by destructive distillation. As a by-product ammonium compounds, such as ammonium sulfate, are obtained. Such shale rocks have been used in Scotland to produce petroleum and ammonium compounds, but in the United States little effort has been made to use our shale deposits. In the future, when our oil wells shall have ceased to supply petroleum in ever-increasing quantities, the oil producers will no doubt develop the shale deposits to secure the oil, with ammonium compounds as by-products for use as fertilizers.

(c) *By the Haber process.* It was known to chemists that some ammonia could be formed by passing an electric spark through a mixture of nitrogen and hydrogen. But the reaction represented by the following equation,



is reversible, and only a small per cent of ammonia is formed. The problem of increasing the percentage of ammonia formed was solved in 1913 by Haber, a German chemist.

He heated the mixture of gases to a temperature of about 500 or 600° C., when they are subjected to a pressure of 200 atmospheres. At first uranium carbide was used as a catalyst, but finely divided iron was found to be as satisfactory. The reaction, which takes place in "bombs" made of special chrome-vanadium steel to withstand the enormous



Courtesy Fixed Nitrogen Research Laboratory

FIG. 128. — Hydrogen and air are introduced in such proportion that there will be 3 volumes of hydrogen to one of nitrogen.

pressure, yields about 8% of ammonia. This ammonia is either absorbed in water or removed by cooling, and the remaining gases are returned to the "bomb" to be exposed again to the action of the catalyst. Without the development of the Haber process, it is doubtful if Germany could have carried on the war for an entire year.

The Fixed Nitrogen Research Laboratory of the United States has succeeded in producing a catalyst that is better than that used in other processes. It consists of a specially prepared mixture of iron, with small percentages of potassium and aluminum oxides. In the Casale process of making ammonia, and in the Claude process, very high pressures are used. (See Fig. 128.) In the latter process, a pressure of 1000 atmospheres is used, and the yield is about 40%.

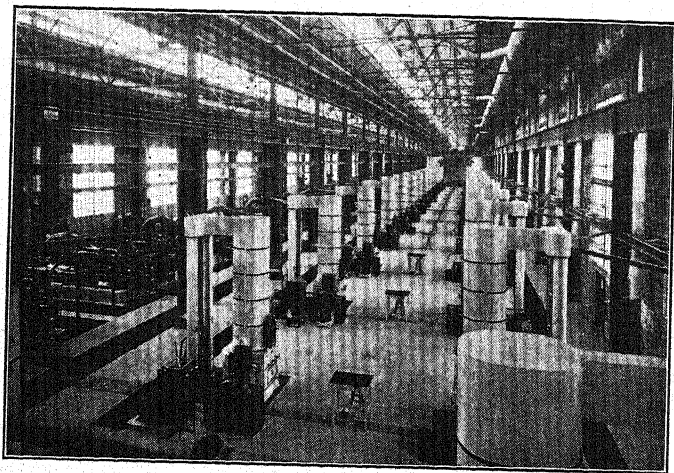
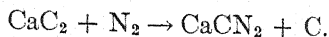


FIG. 129. — Fractionating columns at the Muscle Shoals plant.

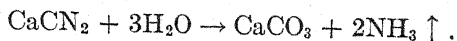
★ (d) *The cyanamide process.* The plant at Muscle Shoals, Alabama, was built during the war to make ammonia by the cyanamide process. Nitrogen is obtained from liquid air by fractional distillation (See Fig. 129), and passed over white



hot calcium carbide. The reaction that occurs is represented by the equation,



In huge autoclaves, such as those shown in Fig. 130, superheated steam interacts with the calcium cyanamide,  $\text{CaCN}_2$ , to form ammonia.



Sometimes the calcium cyanamide is used as a fertilizer without converting it into ammonia.

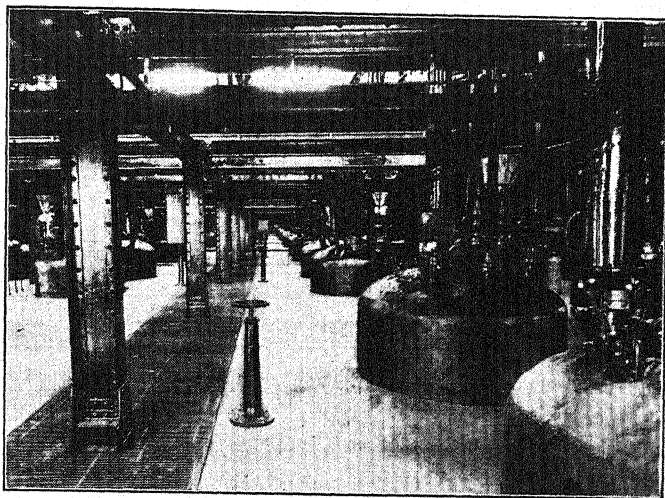


FIG. 130. — In these autoclaves ammonia is formed from calcium cyanamide.

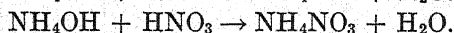
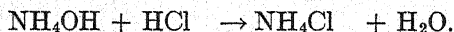
**194. Physical Properties of Ammonia.** Ammonia is a gaseous compound having the formula  $\text{NH}_3$ . It has a peculiar, pungent odor and a bitter taste. Ammonia is lighter than air and very soluble in water. One liter of water

at 20° C. dissolves 710 liters of ammonia gas. At 0° C. one liter of water dissolves almost 1300 liters of the gas. The very high solubility is probably due to a chemical union between the gas and water to form ammonium hydroxide.

The ammonia water thus formed is lighter than water, the specific weight of the 35% solution being 0.88. When ammonia water is boiled the gas is all driven off. Even under ordinary atmospheric pressure, ammonia gas condenses to a liquid when sufficiently cooled. Its boiling point is - 34° C. Liquid ammonia is put on the market compressed in steel cylinders.

**195. Chemical Properties.** Ammonia neither burns nor supports combustion. In oxygen, however, it burns slowly. Heated with copper oxide, it forms water and nitrogen. The water solution of the gas contains a compound having the formula  $\text{NH}_4\text{OH}$ .

The *ammonium*,  $\text{NH}_4$ , group acts as a radical. It combines with the OH radical in water solution, and the compound  $\text{NH}_4\text{OH}$  acts like a base. In this case the  $\text{NH}_4$  radical acts just as the active metals, sodium and potassium, do with the OH radical. Students must never confuse the *ammonium radical*,  $\text{NH}_4$ , with the compound *ammonia*,  $\text{NH}_3$ . While ammonium acts like a metal in compounds, yet it has not been isolated as  $\text{NH}_4$ . It always breaks up into ammonia and hydrogen when it is separated from the negative element or radical with which it was combined. The following equations show the behavior of the ammonium radical,  $\text{NH}_4$ .



**196. Ammonium Salts.** Since ammonium hydroxide acts like a base, we would expect it to form *ammonium* salts. When it unites with hydrochloric acid, it forms a white, crystalline solid known as ammonium chloride,  $\text{NH}_4\text{Cl}$ , often called *sal ammoniac*. This salt is used in dry cells and

as a flux in soldering. When the salt is heated, it decomposes as shown by the reversible equation,



The hydrochloric acid thus liberated by the hot soldering iron dissolves the tarnish on the surface of the metal so the solder will stick to the clean metal.

*Ammonium sulfate*,  $(\text{NH}_4)_2\text{SO}_4$ , is also a white, crystalline salt, easily soluble in water. It is obtained as a by-product in making coal gas, and it finds extensive use as a fertilizer.

★ *Ammonium carbonate*,  $(\text{NH}_4)_2\text{CO}_3$ , is a white, crystalline solid. It is unstable, and gives off ammonia gas slowly. Hence it finds use in *smelling salts*. When this salt is dissolved in alcohol, together with ammonia water and such spicy oils as nutmeg, lemon, and lavender, it forms *aromatic spirits of ammonia*. When inhaled or taken internally, this drug acts as a stimulant.

★ *Ammonium nitrate*,  $\text{NH}_4\text{NO}_3$ , is used in making nitrous oxide,  $\text{N}_2\text{O}$ , a gas used as an anesthetic. Ammonium nitrate is used in coal mines as an explosive. When it is mixed with T. N. T., it forms a powerful explosive, which was much used during the war under the name *amatol*.

**197. Uses of Ammonia.** 1. *As a fertilizer.* Plants must have nitrogen from nitrogen compounds in order to make proteins, without which there can be no life. No compounds are more important as plant foods or fertilizers than ammonia and the ammonium compounds.

2. *As a detergent.* Since aqua ammonia is a base, we would expect it to act upon fats and oils. It is quite extensively used in the household for removing grease spots from rugs and clothing. When the water evaporates, no solid residue is left, because the gas ammonia is liberated to the air at the same time. For this reason, ammonia does not injure fabrics as do such bases as sodium and potassium hydroxides. It may dissolve the dye in colored fabrics.

3. *For refrigeration.* (a) *The physical principle.* If we pour water on one hand and let the water evaporate quickly, that hand will feel cooler than the other. It requires heat to evaporate the water. The heat in this case came from the hand, and such subtraction of heat left the hand cool. If we were to repeat the experiment, using alcohol instead of water, the hand would feel cooler than before. Alcohol has a boiling point of only  $78^{\circ}\text{C}.$ ; hence it evaporates *faster* and takes heat from the hand faster. Ether poured on the hand seems even colder than alcohol as it evaporates. The boiling point of ether is  $35^{\circ}\text{C}.$ , less than blood heat. Does it not seem possible, then, if we were to use a substance like liquid ammonia, which boils at  $-34^{\circ}\text{C}.$ , that heat could be taken from the water surrounding the liquid ammonia as it evaporates, so fast that the water will freeze? To convert 1 gm. of liquid ammonia into gaseous ammonia takes 295 calories of heat. That is its *heat of vaporization*. If we *subtract* 80 calories of heat from 1 gm. of ice water,

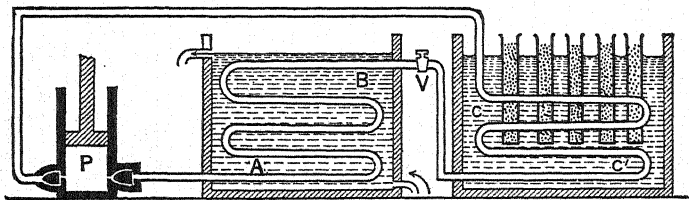


FIG. 131. — Diagram of an artificial ice plant. The coils *AB* are for cooling.

the water will freeze. To make ice, then, one subtracts heat from water by taking its heat and using it to evaporate liquid ammonia. Other liquids that boil at low temperatures are sometimes used.

(b) *The practice.* At ordinary room temperatures, it takes a pressure of only about 4.5 atmospheres to liquefy ammonia. By the use of a compression pump, as shown in Fig. 131

ammonia gas is compressed enough so it will liquefy in one set of pipes around which cold water is kept flowing to absorb the heat liberated as the ammonia liquefies. The liquid ammonia then passes through an expansion valve into a second set of coiled pipes, which are immersed in a tank of *brine*. In this second set of pipes the liquid ammonia evaporates, taking the heat needed for its vaporization from the brine. Thus the brine may be cooled to  $-10^{\circ}\text{C.}$ , or lower. Cans of fresh water immersed in the brine tank will be frozen solid in a few hours.

In cold storage plants, the cold brine is pumped through pipes near the ceiling of the storage room. Just as hot water flowing through pipes may warm a room by radiation and convection, so the circulation of cold brine through pipes cools a room, and may keep it at any desired temperature.

## SUMMARY

*Ammonia* is formed by the decay of animal and vegetable matter. It is prepared in the laboratory by heating some strong base with a salt of ammonium. Slaked lime, or *calcium hydroxide*, is usually heated with *ammonium chloride*.

Commercially ammonia may be obtained as a by-product from the distillation of soft coal. It is also a by-product from the destructive distillation of oil-bearing shale rock. Ammonia is made synthetically by heating nitrogen and hydrogen under pressure in the presence of a suitable catalyst, such as iron with oxides of potassium and aluminum. It can also be made by the cyanamide process by passing nitrogen over white hot calcium carbide, and treating the calcium cyanamide,  $\text{CaCN}_2$ , that is formed with superheated steam.

Ammonia is a colorless gas; it has a very pungent odor. Its odor is so peculiar that it serves as a means of identifying the gas. Ammonia is very soluble in water, and forms a strong base with the water.

Ammonia neither burns nor supports combustion. In the compound ammonium hydroxide, the  $\text{NH}_4$  group acts like a metal, and may combine with acid radicals to form salts.

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The salts of ammonium are generally white crystalline solids, easily soluble in water. The *chloride* finds use in voltaic cells and for soldering. The *sulfate* is a fertilizer, and the *nitrate* is used as an explosive.

Ammonia finds use: (1) as a *fertilizer*; (2) as a *base for cleansing purposes*; (3) as a *refrigerant* for making artificial ice.

### QUESTIONS

#### GROUP A

1. Dry ammonia gas does not affect litmus. Explain.
2. What is the difference between *ammonia* and *ammonium*?
3. Why is *brine* used in the tanks containing the cans of fresh water for making ice?
4. Suppose you were given a compound. How would you test it to see whether it contains the ammonium radical?

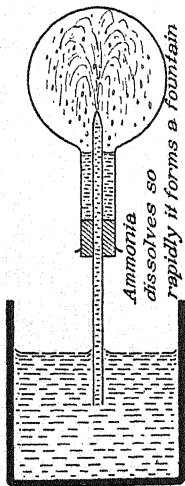


FIG. 132. — Ammonia gas is extremely soluble in water.

5. Why have so much time and money been spent in *fixing* atmospheric nitrogen?
6. How does liquid ammonia differ from ammonium hydroxide? Write the formulas.
7. What simple method can you suggest for preparing a few c.c. of ammonia gas?
8. What are the particles formed by holding the stopper from a bottle of concentrated hydrochloric acid near the stopper from a bottle of concentrated ammonium hydroxide?

#### GROUP B

9. Why is ammonia called the "volatile alkali"?
10. Gases are dried by bubbling them through concentrated sulfuric acid. Can ammonia be dried in this manner? Explain.
11. What is the valence of the nitrogen in ammonia? What is the valence of the nitrogen in ammonium chloride? Write the structural formulas of each one.

12. Write equations to show the interaction of ammonium hydroxide with each of the following acids: sulfuric; carbonic; and phosphoric.

13. Give the names of the salts formed in each case of Question 12.

14. If one fills a flask with ammonia gas, stoppers the flask with a stopper carrying a long jet tube, and then holds the end of the tube in water as shown in Fig. 132, the water slowly rises in the tube and then spurts up into the flask. Explain.

15. What is meant by a "pressure of 1000 atmospheres"?

## PROBLEMS

### GROUP A

1. How many grams of ammonia can be prepared from 40 gm. of ammonium chloride?

2. How many grams of calcium hydroxide are needed to react with 140 gm. of ammonium sulfate?

3. Calculate the per cent of nitrogen in calcium cyanamide. Calculate the per cent of nitrogen in ammonium sulfate.

### GROUP B

4. How many grams of ammonium chloride are needed to prepare 20 liters of ammonia at S. T. P.?

5. In the Haber process how many liters of hydrogen are needed to combine with 500 liters of nitrogen? How many liters of ammonia are formed at S. T. P.? How many liters of water at 0° C. will be needed to absorb the ammonia?

6. How many c.c. of N-HCl will be needed to neutralize 50 c.c. of a solution that contains 10% of  $\text{NH}_4\text{OH}$  by weight?

## SUPPLEMENTARY PROJECTS

1. Prepare a report on the work of the chemists of the Fixed Nitrogen Research Laboratory.

Reference: CHAMBERLAIN, J. S., *Chemistry in Agriculture*. Chemical Foundation, Inc. Chap. 4.

2. Prepare a report on the topic "Chemistry of Refrigeration."

Reference: HOWE, H. E., *Chemistry in Industry*. Chemical Foundation, Inc. Vol. II, Chap. 19.

## CHAPTER 17

# NITRIC ACID AND THE OXIDES OF NITROGEN

### Vocabulary

**Retort.** A closed vessel in which a substance may be heated without access to air.

**Detonator.** An explosive whose action is practically instantaneous.

**Infusorial.** Pertaining to a group of animals; many of them deposit silica as their bodies decay.

**Anesthetic.** A drug that produces insensibility to pain, sometimes with the loss of consciousness.

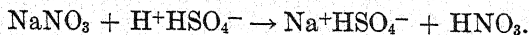
**Siliceous.** Containing silica, or silicon dioxide.

**Adsorb.** To condense on the surface of a substance.

### A. NITRIC ACID

**198. Introductory.** This acid, and the method of preparing it, were described by the alchemist Geber in the eighth century. The early alchemists called it *aqua fortis*, from the Latin words meaning "strong water." Nitric acid, which has the formula  $\text{HNO}_3$ , is one of the strongest acids known.

**199. How Nitric Acid Is Prepared.** 1. *In the laboratory.* In order to prepare nitric acid in the laboratory, we use the general method of preparing acids that we learned in Section 153. In a glass-stoppered retort, sodium nitrate or Chile saltpeter is heated with rather concentrated sulfuric acid. The nitric acid volatilizes, and its vapor is condensed in the tube of the retort and collected in the receiver. (See Fig. 133.) Remembering that sulfuric acid when used in excess furnishes the negative  $\text{HSO}_4^-$  radical, we write the equation as follows:





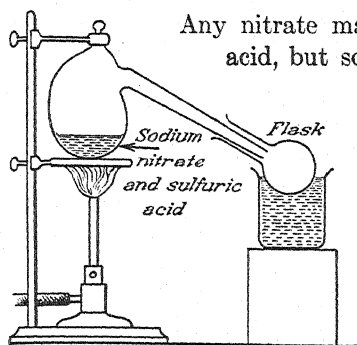


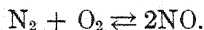
FIG. 133. — Apparatus used for the laboratory preparation of nitric acid.

Any nitrate may be used to prepare nitric acid, but sodium nitrate is the only one that is found occurring in any considerable quantity in nature. The valuable beds of this mineral that occur in the desert regions of Northern Chile have been the cause of the triangular boundary disputes between Chile, Peru, and Bolivia. They were block-

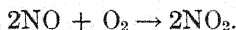
aded by the English navy

during the early part of the World War to prevent supplies from reaching Germany for use in making explosives.

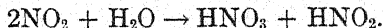
2. *From the air.* When a lightning discharge occurs in moist air, nitric acid is produced. It is estimated that in every month about one pound of nitric acid for every acre of the earth's surface is made in this way. Men have tried to emulate nature. Bradley and Lovejoy used the electric arc at Niagara Falls to produce nitric oxide. After their attempt failed commercially, the Birkeland-Eyde process was developed in Norway. There a large magnet was used to spread the arc and give greater surface. Many tons of nitrate were produced by this process, which is now practically obsolete. At first nitric oxide was formed,



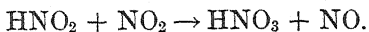
This oxide unites with more oxygen,



The reddish brown nitrogen peroxide dissolves in water as represented by the equation,



The nitrous acid,  $\text{HNO}_2$ , is oxidized to nitric acid by nitrogen peroxide or slowly by air.



3. *Commercial preparation.* (a) *From sodium nitrate.* One method of preparing nitric acid makes use of the same method that is used in the laboratory, heating sodium nitrate with sulfuric acid. Strange as it may seem, this method is the same one that was used by the alchemists more than one thousand years ago. The mixture is heated in iron retorts, and the acid is condensed in large bottles containing a little water.

(b) *From ammonia.* The Haber process made it possible for the Germans during the war to get compounds suitable for fertilizers, but that process alone did not help in the making of explosives. Nitric acid is needed for that purpose. Chemists had known that ammonia may be oxidized to form nitric acid, but it was Ostwald, a German chemist, who made such oxidation of ammonia a commercial success by the use of *platinum gauze* as a catalyst. At a temperature of about  $700^\circ \text{C}.$ , a mixture of ammonia and air is passed through the electrically heated gauze, which is so active as a catalyst that only a small fraction of a second is sufficient to cause the oxidation of a large per cent of the ammonia. A series of reactions takes place, but the equation may be written as follows:

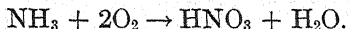


Figure 134 shows the towers that were constructed at Muscle Shoals for the oxidation of ammonia. In Europe several hundred thousand tons of nitric acid are now made annually from the air. While the enormous plant at Muscle Shoals is becoming obsolete, several large private companies in the United States have built plants which are now used to make nitric acid by the oxidation of ammonia.

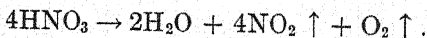
**200. Physical Properties.** Nitric acid is a colorless liquid, more than  $1\frac{1}{2}$  times as heavy as water. The pure acid boils at  $86^{\circ}\text{C}$ . It fumes in moist air. Since the pure acid is unstable, the concentrated nitric acid of commerce is a water solution containing about 68% nitric acid. Such a



FIG. 134. — In these towers ammonia may be oxidized to form nitric acid.

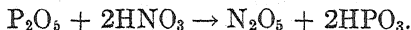
solution boils at  $120^{\circ}\text{C}$ . A more dilute solution boils at a lower temperature and loses water, thus becoming more concentrated.

**201. Chemical Properties.** 1. *Its stability.* When nitric acid is boiled, or even when exposed to sunlight, it decomposes and forms *water*, *oxygen*, and *nitrogen peroxide*. The equation is as follows:



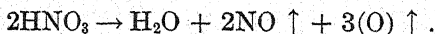
In water solution, the acid is quite stable. The yellow color of nitric acid may be due to the nitrogen peroxide

formed by a decomposition of some of the acid. If the acid contains large quantities of nitrogen peroxide in solution, it will have a red color. It is known as *fuming nitric acid*. It is possible to dehydrate nitric acid and leave a white, crystalline solid, *nitric anhydride*,  $N_2O_5$ . The following equation shows how phosphorus pentoxide may be used for this purpose:



2. *It is an acid.* When nitric acid is *dilute*, it has the properties that are common to acids, as outlined in Section 155. It acts on metals and the oxides of metals and forms *nitrates*. The *concentrated* acid has some remarkable properties.

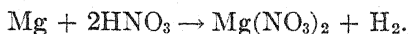
3. *Nitric acid is an oxidizing agent.* If we put about 5 c.c. of concentrated nitric acid in a test tube, clamp it in a slightly inclined position, and slide a loose plug of excelsior down the tube to a position about an inch above the surface of the acid, this plug of excelsior will be ignited when the acid is boiled, and it will unite with the oxygen supplied by the acid. Wool, hair, cotton, and other fibers will burn in a similar manner. Red hot charcoal will burn beneath the surface of the acid, taking the oxygen formed as the acid decomposes. During such oxidation of organic material, of course the nitric acid is reduced. Such products as  $NO_2$ ,  $NO$ ,  $N_2O$ , or  $NH_3$  may be formed by such reduction. It is interesting to observe that the valence of the nitrogen changes from +5 in  $HNO_3$  to +4 in  $NO_2$ , to +3 in  $HNO_2$ , to +2 in  $NO$ , to +1 in  $N_2O$ , to 0 in  $N_2$ , and to -3 in  $NH_3$ . In the presence of a reducing agent, nitric acid often decomposes as represented by the following equation:



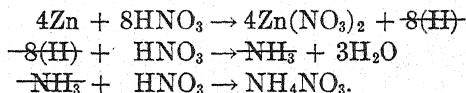
The oxygen atoms, which are available for combining with the reducing agent, are shown in parenthesis. Nitric acid

stains the skin yellow, forming *xantho-proteic acid*. On proteins it produces the same effect; hence it may be used as a *test for protein*.

★ 4. *The action with metals.* How nitric acid reacts with metals will depend upon two things: the *activity* of the metal and the *concentration* of the nitric acid. With such *active* metals as sodium, calcium, or magnesium (see table on page 76), *very dilute* nitric acid will liberate hydrogen and form a nitrate. A typical equation follows:



With a less active metal, such as zinc, the more concentrated nitric acid may at first form some hydrogen, but it immediately oxidizes that hydrogen to form water. No hydrogen escapes. At the same time the hydrogen is reducing the nitric acid to ammonia, which forms some ammonium nitrate with part of the nitric acid. No one can stop a chemical reaction of this kind to determine what happens during the various steps. The *end-products* can be analyzed. Of them we are certain, but we can only *speculate* concerning the intermediate steps. *Partial* equations are often used to show what is believed to occur. For example,



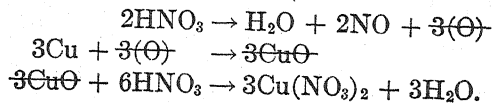
In such partial equations, we may cancel out all the factors and products that are common to both sides of the series of equations. That is, we cancel out the hydrogen, because it probably reduces the nitric acid; and the ammonia, because it probably combines with a part of the nitric acid. Now if we add all the uncanceled factors and all the uncanceled products we get the final equation, which represents the *end* reaction.



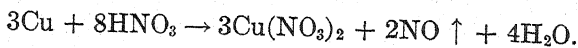
## 270 NITRIC ACID AND OXIDES OF NITROGEN

These partial equations and the final equation are too difficult for beginning students. They are for illustration only, and not to be remembered.

When a less active metal, such as copper, interacts with *moderately* concentrated nitric acid, the reduction of the acid is not so complete. Let us represent by *partial* equations the possible series of reactions:



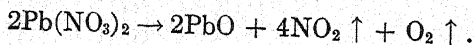
By cancelling the factors and products common to both sides, and combining the uncanceled terms, we have the following:



It is possible that the nascent oxygen, formed by the decomposition of some of the nitric acid, attacks the copper and forms copper oxide, which in turn interacts with the excess acid to form copper nitrate. Such very inactive metals as gold and platinum are not attacked by nitric acid at all, and aluminum is only slightly affected. All other *common* metals are attacked by nitric acid, and *nitrates* are formed, except in the case of tin.

**202. Nitrates.** The nitrates of the various metals are all crystalline compounds, easily *soluble in water*. Therefore, they cannot be prepared by precipitation. They are much used in chemical laboratories when one wishes to work with a soluble salt of a metal.

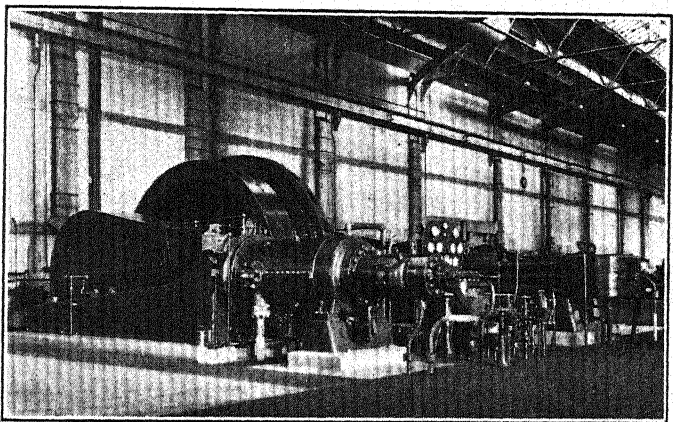
In general, when the nitrate of a metal is heated, the oxide of the metal is formed, and both oxygen and nitrogen peroxide are liberated as gases. The decomposition of lead nitrate is typical of such reactions:





*Courtesy of E. I. DuPont de Nemours & Co.*

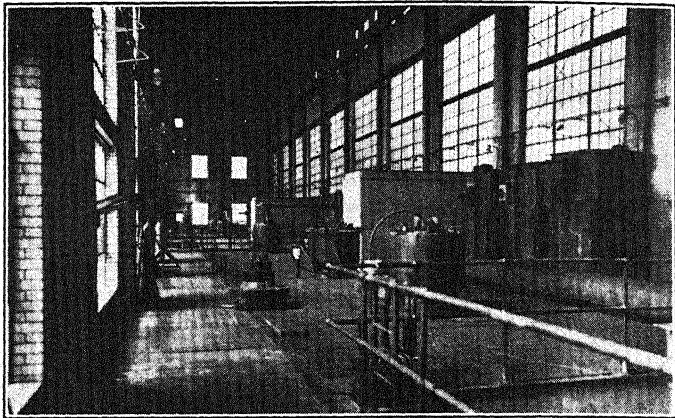
A general view of a synthetic ammonia plant at Belle, West Virginia. Hydrogen, obtained from water gas, is mixed with nitrogen and the two are synthesized in the large building in the center foreground.



*Courtesy of E. I. DuPont de Nemours & Co.*

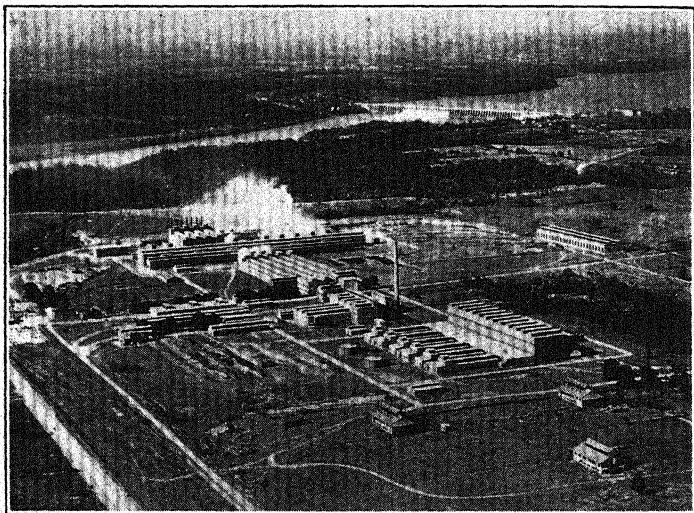
By the use of such compressors the nitrogen-hydrogen mixture is synthesized under a pressure of 900 atmospheres.





*Courtesy of E. I. DuPont de Nemours & Co.*

This room shows the tops of the alloy steel reaction tubes in which the synthesis of the ammonia occurs. The boxlike apparatus at the right contains the cooling coils.



*Brown Bros.*

An air view of Nitrate Plant No. 2 with Wilson Dam in background. A plant was built here by the Tennessee Valley Authority for experimental production of fertilizers.



The nitrates of the active metals, sodium and potassium, react differently when they are heated. Sodium nitrate, for example, yields *sodium nitrite* and oxygen.



**203. How to Test for Nitrates.** To the solution to be tested, one adds a concentrated solution of freshly prepared *ferrous sulfate*,  $\text{FeSO}_4$ . To the mixture, a few c.c. of concentrated sulfuric acid are so added that the heavy acid will run down the inclined tube containing the mixture, but not mix with it. At the intersurface of the acid and the mixture, a *brown ring* will be formed, if the unknown solution contained a nitrate. When carried out properly, this forms a very sensitive *test for a nitrate*.

**204. What Is Aqua Regia?** Such metals as gold and platinum are not affected by ordinary single acids, but they dissolve in a mixture of nitric and hydrochloric acids known as *aqua regia*. This mixture was so named because it dissolves gold, the king (*rex*) of metals from the alchemist's point of view. The name comes from the Latin, and means "royal water."

The nitric acid serves as an oxidizing agent, attacking the hydrochloric acid, and liberating *nascent chlorine*. The chlorine attacks the metal, and a *chloride* is formed instead of a nitrate. Generally, the mixture consists of 1 part of nitric acid to 3 parts of hydrochloric acid, but other proportions may be used.

**205. Uses of Nitric Acid.** 1. *To prepare nitrates.* We have already learned that nitric acid is used to prepare nitrates, by its interaction with metals or metallic oxides. Its salts are used as fertilizers.

2. *In the dye industry.* There are several products obtained from coal tar with which nitric acid will interact to form such *nitro-compounds* as *nitro-benzol*,  $\text{C}_6\text{H}_5\text{NO}_2$ . When this compound is treated with nascent hydrogen

it forms *aniline*, a compound used in making many different dyes.

3. *In making "artificial silk."* Enormous quantities of nitric acid are now being used to nitrate cotton and produce silk substitutes. The processes used are discussed under cellulose.

4. *In making plastics.* The chemical nature of such plastics as *pyralin* and *celluloid* is not very different from that of some of the silk substitutes. Cotton is treated with a mixture of nitric and sulfuric acids, and the nitrated cellulose is treated with camphor and dissolved in certain alcohols or organic solvents, to make a plastic substance that can be rolled, cut, or pressed into any desired shape. *Lacquers* of the Duco type are made in a similar manner from nitro-cellulose.

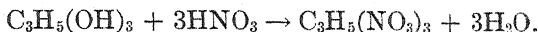
5. *In making explosives.* The use of nitric acid in making explosives is so important that modern warfare could not be waged without it. Some of the more common explosives are discussed in the following sections.

#### \* B. EXPLOSIVES

206. **What Is Black Gunpowder?** Centuries before gunpowder was used in Europe it is said to have been known in China. As early as the first part of the fourteenth century it appeared in Europe. Gunpowder is made by mixing 75 parts of potassium nitrate with 15 parts of charcoal and 10 parts of sulfur. The powdered mixture is moistened and pressed into a cake by means of a hydraulic press. It is then broken up into grains of the desired size. Gunpowder is used as a *priming* charge in firing the so-called "smokeless powder."

207. **Nitroglycerine a Powerful Explosive.** This explosive was discovered by Sobrero in 1846, but it was not developed until 16 years later when Nobel devised a practical method of making it. It is said that Nobel founded the

"Peace Prize" when he realized the possibilities for evil in certain explosives he had invented. *Nitroglycerine*, or *glyceryl nitrate*, is made by treating glycerine with a mixture of nitric and sulfuric acids. The sulfuric acid absorbs the water as it is formed, and prevents the dilution of the nitric acid.



Nitroglycerine is a heavy, oily liquid. In the open air it burns readily. Since one molecule has more than enough oxygen to combine with all its carbon and hydrogen, it burns without access to air, forming water vapor, carbon dioxide, nitrogen, and oxygen. Such compounds are said to explode by *detonation*. Since the gases that are formed occupy many times the volume of the explosive, tremendous pressure is exerted by the decomposition of such explosives.

**208. How Dynamite Is Made.** This explosive was invented in 1866 by Alfred Nobel. Infusorial earth consists of the microscopic skeletons of certain one-celled animals. This siliceous matter will adsorb from 40% to 75% of nitroglycerine, thus forming *dynamite*. Wood pulp is also used as an adsorbent. Sticks of dynamite are much safer to handle than the liquid nitroglycerine.

**209. What is Nitrocellulose?** In 1846 guncotton, or nitrocellulose, was prepared by Schönbein. Cotton fibers consist of nearly pure cellulose,  $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ . When nitric acid acts on cotton, a series of nitrates is formed. A mixture of *concentrated* nitric and sulfuric acids acts on cotton forming *cellulose hexa-nitrate*,  $\text{C}_{12}\text{H}_{14}\text{O}_4(\text{NO}_3)_6$ . More *dilute* acid gives lower nitrates of cellulose. For use in making smokeless powder, the acid is made just strong enough to give a nitrate of cellulose that contains a little less than 13% nitrogen. With ether such a nitrate forms a plastic mass which may be pressed into various shapes and cut into different-sized

grains of powder. (See Fig. 135.) The smokeless powder produces carbon dioxide, carbon monoxide, water vapor, and nitrogen when it burns. Since these are all gaseous, no smoke is produced. This powder is also superior to the black

gunpowder because it is more powerful, thus making a gun more efficient with a smaller weight of ammunition.

The lower nitrates of cellulose dissolve readily in a mixture of alcohol and ether, forming *collodion*. It is used in surgery as liquid court plaster, or "New Skin." Collodion also finds use in photography, and in making picture films.

*Blasting gelatine* is an exceedingly powerful explosive made by dissolving nitrocellulose in nitroglycerine. The names "nitrocellulose" and "nitroglycerine" are not strictly correct. It is more accurate to speak of them as *cellulose nitrate* and *glyceryl nitrate*.

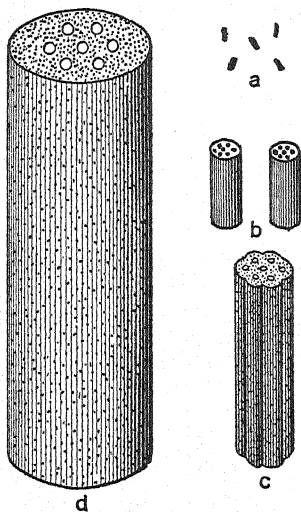


FIG. 135. — Grains of smokeless powder. a. Rifle powder. b. For 3-in. gun. c. For 6-in. gun. d. For 12-in. gun. (Actual size.)

**210. Picric Acid** is a yellow crystalline solid that is made by the action of nitric acid on *phenol*, or *carbolic acid*,  $C_6H_5OH$ . It is a tri-nitro-phenol having the formula  $C_6H_2OH(NO_2)_3$ . Picric acid and its salts are very explosive. It is a favorite explosive with the French, being used under the names *lyddite* and *mellinite*.

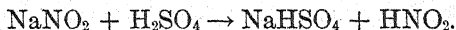
**211. Tri-nitro-toluol (T. N. T.)** is a comparatively new explosive that was introduced just a short time before the beginning of the late war. It is made by treating *toluol*,  $C_7H_8$ , a coal-tar product, with a mixture of nitric and sulfuric

acids. It has the formula  $C_7H_5(NO_2)_3$ . T. N. T. is a colorless solid which darkens upon exposure to air. It cannot be used as a powder, but it is a very satisfactory explosive for use in hand grenades, high explosive shells, depth bombs, torpedoes, and mines. It can be melted with safety and poured into the shells.

**212. Mercury Fulminate**, or fulminating mercury, is sometimes used as a *detonator*. For exploding any kind of powder or high explosive a small cap or cartridge is filled with mercury fulminate. The fulminate explodes with a sudden shock and thus causes the powder to explode by detonation. This compound,  $HgC_2N_2O_2$ , is made by treating mercury with nitric acid in the presence of alcohol. It is one of the most treacherous of explosives, since it may be exploded by heat, shock, or friction. While the chemistry of explosives seems very simple, the technique is complicated, and *no amateur should ever try to make any explosive*.

### C. NITROUS ACID AND NITRITES

★ **213. Nitrous Acid and Nitrites.** We have learned that sodium nitrite is formed when sodium nitrate is heated. *Nitrites* are salts of *nitrous acid*,  $HNO_2$ , an unstable acid of relatively small importance. It can be made by treating a nitrite with sulfuric acid.



These compounds find some use in the manufacture of dye-stuffs.

### D. THE OXIDES OF NITROGEN

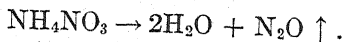
**214. The Five Oxides of Nitrogen.** Although nitrogen does not unite easily with oxygen, yet it is possible, directly or indirectly, to form five different oxides, because the valence of nitrogen varies from 1 to 5. *Nitrous oxide* has the formula  $N_2O$ ; *nitric oxide* has the formula  $NO$ ; *nitrogen trioxide*,

## 276 NITRIC ACID AND OXIDES OF NITROGEN

$N_2O_3$ , is the anhydride of nitrous acid; *nitrogen dioxide*, more commonly called *nitrogen peroxide*, has the formula  $N_2O_4$  at a low temperature, and the formula  $NO_2$  at a higher temperature; *nitrogen pentoxide*,  $N_2O_5$ , is the anhydride of nitric acid. The anhydrides of nitrous and nitric acids have been mentioned. They are oxidizing agents.

**215. What Is Nitrous Oxide?** The compound,  $N_2O$ , is commonly called *laughing gas*, because one who inhales it is likely to burst out into fits of hysterical laughter. After Davy discovered the peculiar property of this gas, it became a fad to administer it at social gatherings in London, merely as a source of amusement.

1. *Its preparation.* When *ammonium nitrate* is heated, it decomposes into water and nitrous oxide, as represented by the equation,



The gas is generally collected by water displacement. The student should compare this equation with the one for the making of nitrogen.

2. *The properties of nitrous oxide.* This gas is colorless, but it has a sweetish odor and taste. It is heavier than air, and moderately soluble in water. It is easily liquefied, and it is usually sold in steel containers.

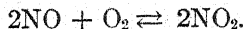
At ordinary temperatures, nitrous oxide is stable, but at slightly increased temperatures it decomposes into nitrogen and oxygen. When such decomposition occurs, the resulting mixture of gases (2 to 1) is richer in oxygen than air (4 to 1). Hence nitrous oxide supports combustion better than air does, provided the burning substance is hot enough to decompose the gas. A *glowing* splinter bursts into flame and burns almost as fast as in oxygen. We can tell this gas from oxygen, however, because *barely ignited, feebly burning* sulfur will be extinguished in it, but not in oxygen. *Vigorously* burning sulfur will continue to burn in either one.

3. *Uses of nitrous oxide.* Although Davy noticed the peculiar properties of nitrous oxide more than 40 years before, it was not used as an anesthetic until 1844, when Dr. Horace Wells, of Hartford, Conn., began to use it when extracting teeth. Wells is really the "father of anesthesia." When used by dentists, oxygen is usually administered with it. Some surgeons start with nitrous oxide before they administer ether.

216. Nitric Oxide, NO. 1. *Preparation.* In our study of the properties of nitric acid, we learned that this gas is set free when moderately concentrated nitric acid acts on copper. The gas is collected by water displacement.

2. *Properties of nitric oxide.* This gas is colorless and slightly heavier than air. It is only slightly soluble in water.

The most important chemical property of nitric oxide is its ability to unite directly with more oxygen to form *nitrogen peroxide*. Figure 136 shows how the reddish-brown gas, nitrogen peroxide, is being formed upon exposure of nitric oxide to air. The equation for the reaction follows:



This is the reaction that occurs when a lightning discharge passes through moist air during a thunderstorm.

Nitric oxide is quite stable. Although it is more than 50%

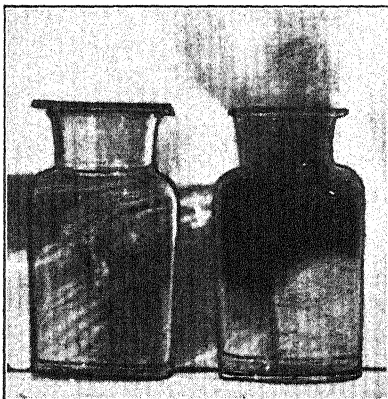
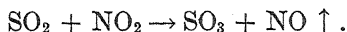


FIG. 136. — The colorless nitric oxide unites with oxygen to form the reddish-brown nitrogen peroxide.

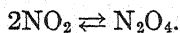
oxygen, it will not support ordinary combustion. Vigorously burning phosphorus is hot enough to decompose it, and burn in it very rapidly.

3. *Uses of nitric oxide.* The ease with which nitric oxide takes on oxygen from the air and then gives it up again in the presence of a reducing agent makes this gas a valuable *carrier of oxygen*. For example, nitric oxide forms the peroxide,  $\text{NO}_2$ , upon exposure to air. The peroxide oxidizes sulfur dioxide as shown in the equation,



The nitric oxide that is produced at the same time may take on more oxygen and in turn oxidize more sulfur dioxide. This property of nitric oxide is used in the manufacture of sulfuric acid. (See Section 326.)

**217. Nitrogen Peroxide or Tetroxide,  $\text{NO}_2$ .** In the preceding section we learned that nitrogen peroxide is formed when nitric oxide is exposed to the air. It may be formed by heating nitrates, sodium, potassium, and ammonium nitrates excepted. At ordinary temperatures it is a reddish-brown gas, having a disagreeable suffocating odor. *This gas is very poisonous.* Its molecular weight shows that its formula is  $\text{NO}_2$ . At low temperatures the color practically disappears and the molecular weight increases, showing that it has the formula  $\text{N}_2\text{O}_4$ . Such *association of molecules* at low temperatures and *dissociation* at higher temperatures is not uncommon in chemistry. The reversible equation follows:



Nitrogen peroxide is unstable enough to support ordinary combustion very readily. It is very soluble in water, nitric acid being formed by such solution. (See Section 199.)

Nitrogen peroxide is a very useful oxidizing agent. It loses oxygen in the presence of a reducing agent and the nitric oxide formed may take on more oxygen.



## SUMMARY

*Nitric acid*, a strong acid called *aqua fortis*, is prepared by heating a mixture of *sodium nitrate* and *sulfuric acid*. When a lightning discharge occurs in moist air, some nitrogen and oxygen unite to form *nitric oxide*, which immediately unites with more oxygen to form *nitrogen peroxide*, which dissolves in water and forms *nitric acid*. This acid is prepared by the *oxidation of ammonia*.

Nitric acid is a heavy, colorless liquid; it boils at  $86^{\circ}\text{C}$ . In water solution the acid is fairly stable. In very dilute solution it may act as an acid. In concentrated solution it is a vigorous oxidizing agent. Nitric acid seldom liberates hydrogen when it acts on metals; it usually liberates *nitric oxide* or *nitrogen peroxide* and forms nitrates of the metal.

The nitrates are all water soluble. When heated they decompose, and form oxygen or oxides of nitrogen. They find use as fertilizers.

To test for a nitrate, mix the unknown solution with a concentrated solution of freshly prepared ferrous sulfate, and add concentrated sulfuric acid, letting it run down the side of the inclined tube. A brown ring formed at the junction of the two liquids shows that the unknown solution contained a nitrate.

*Aqua regia* is a mixture of hydrochloric and nitric acids that will dissolve some metals that are not acted upon by single acids. The salt formed is a *chloride*.

Nitric acid is used: (1) to prepare nitrates; (2) in the dye industry; (3) in making "artificial silk"; (4) in making plastics; (5) in making explosives.

Practically all modern explosives are made by the action of a mixture of nitric and sulfuric acids on such substances as cotton, glycerine, carbolic acid, or toluol. They are nitrates or nitro-compounds of these substances.

*Nitrous acid* and the *nitrites* find use in the dye industry, and to some extent medicinally.

Nitrogen forms a series of five oxides. *Nitrous oxide*,  $\text{N}_2\text{O}$ , is used as an anesthetic; *nitric oxide*,  $\text{NO}$ , is a carrier of oxygen; *nitrogen peroxide*,  $\text{NO}_2$ , is a vigorous oxidizing agent. The other two are not very important.

## QUESTIONS

## GROUP A

1. Why does nitric acid acquire a yellow color when exposed to sunlight?
2. Explain why modern warfare would be practically impossible without nitric acid.
3. Explain why life would soon cease to exist without nitric acid and the compounds of nitrogen.
4. If you spilled some concentrated nitric acid on your hands, what should you do?
5. How would you neutralize acid stains on clothing? Is the method satisfactory for removing spots made with nitric acid?
6. Given five unlabeled jars containing the following gases: oxygen, nitrogen, nitrous oxide, nitric oxide, and nitrogen peroxide. How would you identify each one?
7. The colonists who settled at Jamestown grew one crop after another of tobacco. Explain how they were robbing their soil of its fertility.
8. If you inherited a farm that had been robbed of its fertility, how should you proceed to build it up again?
9. How would you test the white of an egg for protein?
10. If you had a sample of metal that contains both silver and gold, how could you separate the silver from the gold?
11. In 1898 Sir Wm. Crookes gave a pessimistic lecture in which he predicted a food famine when our nitrate supplies would become exhausted. Do you think there is need to worry now? Explain.

## GROUP B

12. Make a list of the uses of explosives for industrial (non-warfare) purposes.
13. If you had been a United States Senator from your state in 1920, what action would you have undertaken concerning the Muscle Shoals plant?
14. Since nitric oxide has a larger per cent of oxygen in it than nitrous oxide has, why is the latter the better supporter of combustion?

15. Do you think that nitric acid would give a brown ring which is characteristic of the test for nitrates? Is nitric acid a nitrate? Explain.

16. Explain what is meant by each of the following: *aqua fortis*; *aqua ammonia*; *aqua regia*.

17. Why cannot nitric acid be used with zinc in the preparation of hydrogen?

18. What law is exemplified by the oxides of nitrogen? State the law as concisely as you can.

19. What is meant by detonation? Why is it necessary to use a detonator with other explosives?

20. Do you think that you could prepare nitric acid by the interaction of silver nitrate and sulfuric acid? Explain.

21. How can one determine that nitrogen peroxide has the formula  $\text{NO}_2$  at high temperatures, and  $\text{N}_2\text{O}_4$  at low temperatures?

22. Look up the origin of the word "fulminate" and then tell whether you think fulminate of mercury is a suitable name.

## PROBLEMS

### GROUP A

1. A sample of sodium nitrate is 90% pure. How many pounds of nitric acid can be made from one ton of the nitrate?

2. A sample of potassium nitrate is 90% pure. How many pounds of nitric acid can be made from one ton of the nitrate? If sodium nitrate and potassium nitrate were the same price per pound, which would you use in the manufacture of nitric acid?

### GROUP B

3. How many liters of nitric oxide can be prepared by the action of 252 gm. of nitric acid on an excess of copper?

4. If the air were 20% oxygen, in what proportions should air and ammonia be mixed to oxidize ammonia to nitric acid?

5. In what proportions should the air and nitric oxide be mixed to prepare nitrogen peroxide?

6. How many liters of nitrous oxide can be prepared by heating 500 gm. of ammonium nitrate?

## CHAPTER 18

### CARBON

#### Vocabulary

**Amorphous.** (*a*, "without"; *morphe*, "form.") Without crystalline form.

**Refractory.** A substance that does not melt easily.

**Abrasive.** A hard substance used for cutting, grinding, or polishing.

**Deflocculated.** (*de*, "from" or "without"; *floccus*, "flake.") Without lumps or flakes.

**Erosion.** Wearing away by flowing gases or liquids.

**Friable.** (Fr. *friare*, "to crumble.") Easily crumbled to a powder.

**Lubricant.** A substance used between the moving parts of machinery in order to reduce friction.

**218. Carbon in Almost Everything.** The element carbon is not quite omnipresent, but we find it in our fuels, in gasoline, in lubricating oils, in wood, in paper, in our textile fibers, in the tissues of our body, and in our foods. When the potatoes scorch, the meat burns, or the vegetables get too hot, the presence of carbon is shown by the black color that is evident. In all the substances just mentioned, the carbon is present in the combined form, usually united with hydrogen, or with hydrogen and oxygen. In this chapter we shall study carbon as *free* or *uncombined*.

**219. Carbon Occurs in Different Forms.** In our study of oxygen, we learned that oxygen may absorb energy and become more active in the form of ozone. Carbon, too, may exist in different *allotropic* forms. (1) In a beautiful, crystallized form pure carbon exists in the *diamond*. (2) In another crystalline form, less beautiful but more useful, we find carbon as a grayish-black substance called *graphite*.

(3) By the heat treatment of many substances that contain carbon, a non-crystalline, *amorphous* residue of carbon is left. We are familiar with such forms of carbon in *charcoal*, *coke*, *lampblack*, and *boneblack*.

**220. The Diamond — the Hardest Natural Substance.** Kimberley, South Africa, is well known in motion picture and in story for its diamond mines. The Cullinan diamond, taken from those mines, weighed about one and one third pounds. It is the largest ever found. In the rough, the diamond does not have the shape or luster that we know, but to give it that appearance it must be cut and polished.

The diamond is the densest and the hardest form of carbon. It is about 3.5 times as dense as water. Its value as a gem depends upon its ability to reflect and refract light. It has the highest known index of refraction, nearly 2.5. The skilled cutters of Holland, Belgium, and New York know how to cut the diamond to enhance its beauty by an increased play of colors from numerous facets.

The diamond is insoluble in ordinary reagents. By burning a diamond in oxygen, it may be shown that it is composed of pure carbon, because nothing but carbon dioxide is formed. Since diamonds are formed by crystallization under pressure, Henri Moissan, a French chemist, conceived the idea of making them. He dissolved carbon in molten iron, its only solvent. Then he plunged the molten iron into a bath of melted lead to cool it quickly. The iron cooled first on the outside and contracted, producing tremendous pressure upon the inside. When the mass was broken open, some *small* diamonds were found inside. The only sad part of the story lies in the fact that one needed a good microscope to find them.

**221. Uses of the Diamond.** The use of the diamond as a gem is known to all. The carat is the unit weight used. It equals 200 milligrams. But its great hardness makes it useful for several other purposes. Figure 137 shows a saw fitted

with diamonds that serve as teeth. It is used for sawing marble. A chip diamond may be used to cut glass; it may be used as the point in place of a steel phonograph needle. Diamonds are also pierced and set in a brass disc to be used

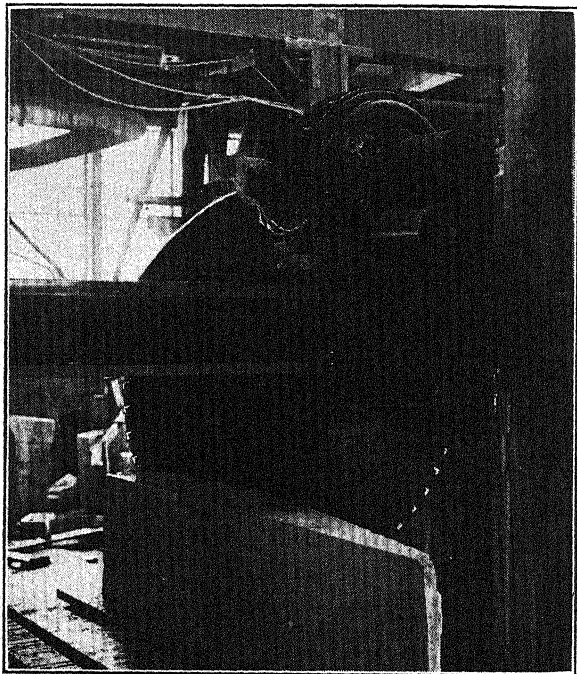


FIG. 137. — A saw fitted with diamond teeth for sawing marble.

as dies for drawing fine wire. Tungsten wire, to be used for electric light filaments, is made by pulling it through a small hole in such a diamond die. It may be drawn so fine that its diamond is about  $\frac{1}{6}$  that of the average human hair.

The black diamond, found in Brazil, is not suitable for gems. It is used extensively by mining prospectors in the

diamond drill. A steel shoe, set at the end of a pipe about  $1\frac{1}{2}$  in. in diameter, is studded with black diamonds. As this drill is turned by machinery, it will cut its way down through the hardest rock. The core that is cut out by the drill is brought to the surface, where it may be examined and analyzed. In that manner, engineers and prospectors can get a good idea of the extent and the richness of beds of ore as they lie several hundred feet underground.

**222. The Electric Furnace.** In order to melt the iron and the charcoal, Moissan used the electric furnace. The simplest form of such a furnace consists of two carbon rods

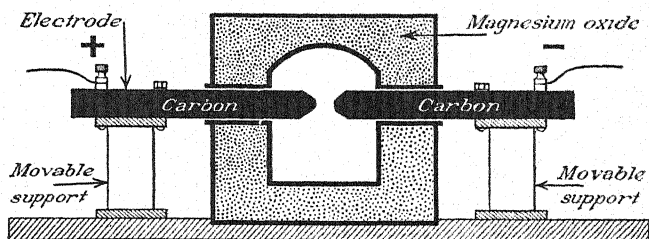
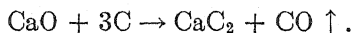


FIG. 138. — A simple electric furnace. The arc formed between the two carbons gives a temperature of  $3500^{\circ}\text{C.}$ , or more.

mounted in a block of refractory material. (See Fig. 138.) When the carbon rods, which serve as electrodes, are brought together momentarily, the heat produced by the electric current vaporizes some of the carbon and forms an arc of carbon vapor. This vapor continues to conduct the current after the rods have been slightly separated. The temperature is very high, estimated at about  $3500^{\circ}\text{C.}$  Several chemical reactions take place at this high temperature that cannot be brought about in any other way.

Some of the products of the electric furnace include the following: *carbon disulfide*,  $\text{CS}_2$ ; *carbon tetrachloride*,  $\text{CCl}_4$ ; *calcium carbide*,  $\text{CaC}_2$ ; *artificial graphite*,  $\text{C}$ ; "*Carborundum*,"  $\text{SiC}$ ; and *high grade steel*. Figure 139 shows an electric

furnace that is used for making calcium carbide. When lime and coke are heated in such a furnace, the reaction that occurs may be represented as follows:



"*Carborundum*," an excellent abrasive, is made in a similar manner by heating sand and coke in an electric furnace.

223. Graphite — a Soft Form of Carbon. While the diamond is the hardest natural substance known, graphite is

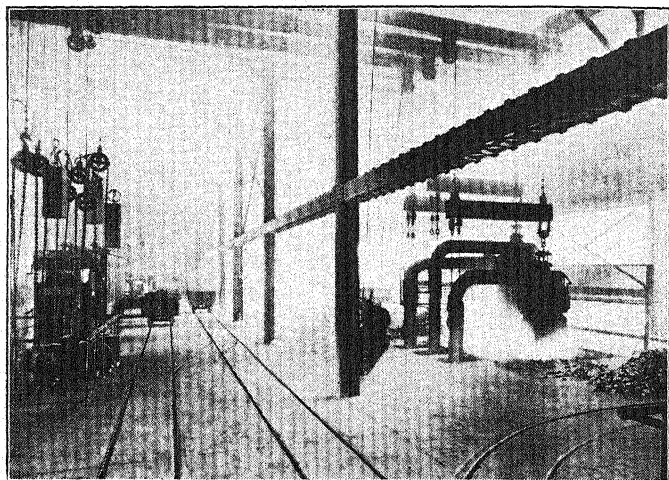


FIG. 139. — An electric furnace used for making calcium carbide.

so soft that it may be scratched by the thumb nail. It is also a crystalline form of carbon; it is friable, and has a greasy feel. Its specific weight is about 2.25. It is quite a good conductor of electricity, although a non-metal. Like the diamond, it does not dissolve in ordinary reagents, and it forms nothing but carbon dioxide when it burns in oxygen.

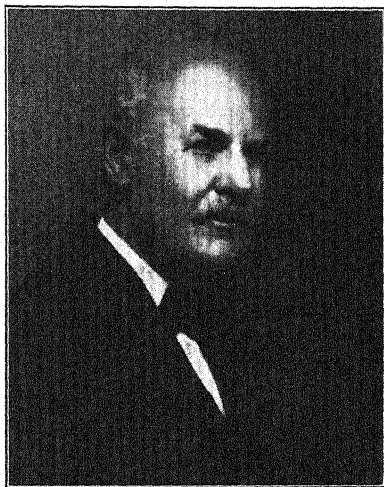
New York and Pennsylvania supply some graphite, but the best graphite comes from Ceylon and Siberia. Acheson,



an American chemist, conceived the idea of making graphite. (See Fig. 140.) He learned that graphite is formed when the vapor from carbon condenses. By heating hard coal or coke in an electric furnace, graphite of good quality is now manufactured. (See Fig. 141.) It was Acheson, too, who first made carborundum. A furnace used for making graphite is shown in longitudinal section in Fig. 142.

**224. The Uses of Graphite.** 1. *As a lubricant.* Every boy has used a stick of graphite to grease his bicycle chain. If oil were used on such a chain, dust would stick to it and cut the metal away rapidly. The dust does not adhere to graphite so readily. At high temperatures, some oils used as lubricants will decompose or vaporize. Graphite makes an excellent lubricant for use at high temperatures, because it is non-volatile.

Acheson learned how to sub-divide graphite into such fine particles that they do not settle when mixed with water or oil. An emulsion of such particles in water is known as *aquadag* (*aqueous deflocculated Acheson graphite*;) *oildag* and *gredag* are names given respectively to suspensions of finely divided graphite in oil and grease. They are all good lubricants. Sometimes graphite is added to smokeless powders to reduce the friction in the gun and decrease erosion.



*Courtesy Acheson Oildag Corp.*

FIG. 140. — Edward Goodrich Acheson (1856-) is an American chemist who was awarded the Count Rumford medal and the Perkin Research Medal for his invention of carborundum, artificial graphite, and siloxicon.

2. *As a refractory.* The melting point of graphite and the temperature at which it vaporizes are practically identical, about  $3500^{\circ}\text{C}$ . If graphite is mixed with some binder to hold

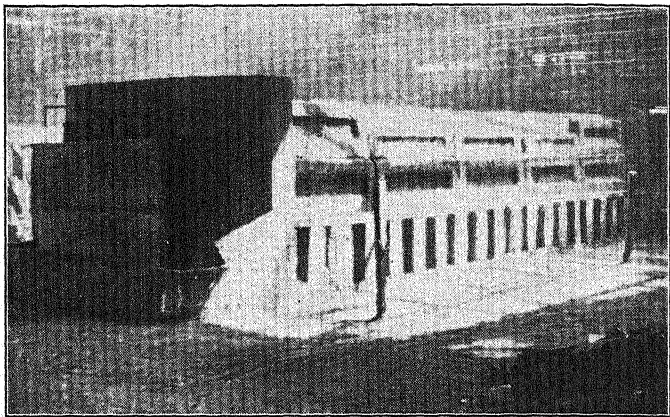


FIG. 141. — Electric furnace for making graphite.

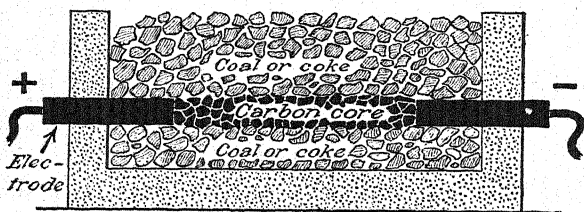
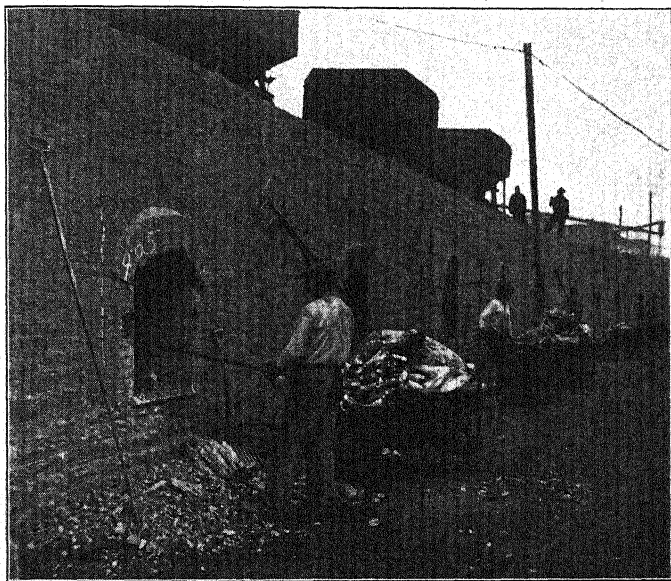


FIG. 142. — Sectional view of a furnace for making graphite.

the particles together, it makes excellent crucibles to be used for high temperature work.

3. *As a conductor.* The wax impression used for making electrotypes is dusted with graphite to make it a conductor. Graphite also finds use for making the electrodes used in electric furnaces. Some electrodes as large as 17 in. in diameter are made for such use.

of adsorbing gases in large quantity is the most remarkable physical property of charcoal. For example, 1 cu. in. of freshly prepared charcoal will adsorb 90 cu. in. of ammonia gas. When poison gases began to be used during the war, chemists tried making charcoal from other materials



*Courtesy United States Steel Corp.*

FIG. 145. — Removing coke from bee-hive ovens. These ovens are obsolete now and the by-product ovens are displacing them. In some places such ovens extended for half a mile in an unbroken line.

to try to find some that are more adsorptive. They learned that charcoal made by heating cocoanut shells, the stones from such fruits as peaches and prunes, and the shells of nuts, adsorbs about 9 times as much gas as ordinary charcoal made from willow. Such charcoal was *activated* for use in gas masks. (See Fig. 144.) *Soda lime* was added to destroy some poisonous gases. As other poisonous gases made their

appearance, the chemists for the defense added to the activated charcoal such chemicals as *sodium phenylate*, *sodium permanganate*, *copper sulfate*, *hexamethyleneamine*, and the oxides of certain metals in order to neutralize the poisonous gas or to destroy its toxicity.

Chemically charcoal is inert at ordinary temperatures. It is insoluble in ordinary reagents. It vaporizes at about

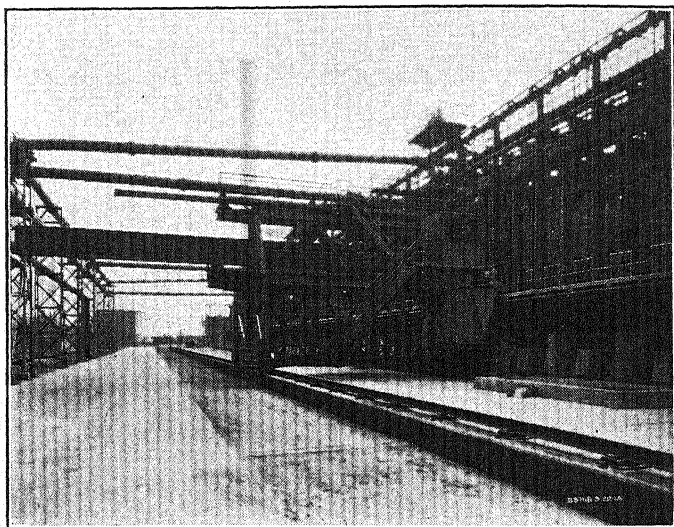


FIG. 146. — Battery of by-product coke ovens.

3500° C. At a high temperature, it unites with oxygen. Thus it is a *reducing agent*.

Charcoal finds some use as a fuel and as a reducing agent. Since it adsorbs gases so readily, it is a good deodorizer. It is also used to decolorize some liquids.

**227. Coke.** If we heat a piece of soft coal in a hard glass tube, we can drive off quantities of *coal gas*, *coal tar*, and *ammonia*. The residue left in the tube is *coke*. Prior to 1914, more than 75% of all the coke made in the United States was

made in *bee-hive* ovens (Fig. 145). In such an oven part of the coal is burned to supply the heat needed to drive off the volatile matter from the unburned portion. It is estimated that the waste in 1913 from the ammonia, the gas, and the coal tar which were driven off into the air and never recovered amounted to \$70,000,000.

The World War helped to teach us to conserve our natural resources. The ammonia is a valuable fertilizer; the coal is a

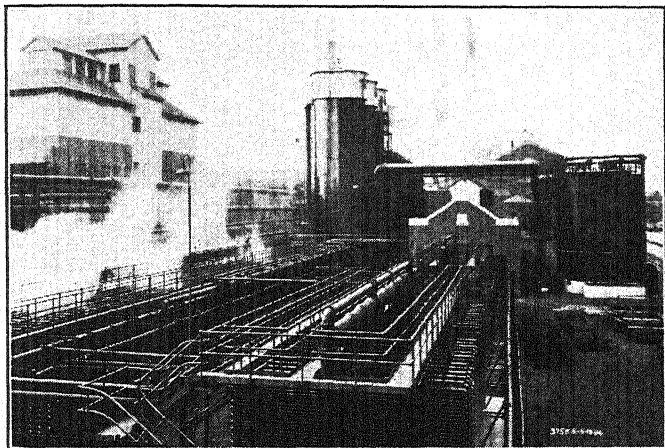


FIG. 147. — These towers, tanks, stills, and condensers conserve for one company 26,000,000 cu. ft. of gas per day; 18,000 gals. of benzol; 60,000 lb. of ammonium sulfate; 17,800 lb. of tar; and 4500 gals. of refined oil.

splendid fuel; and from coal tar the chemist makes drugs, dyes, and explosives. Now more than 95% of the 50,000,000 tons of coke produced annually in the United States is made in by-product coke ovens of the type shown in Fig. 146. Such ovens save the volatile by-products and increase the yield of coke from 10% to 15%. Figure 147 shows a net-work of pipes and condensers used to recover ammonia, tar, gas, and oil in the distillation of soft coal.

Coke is a gray solid, harder and denser than charcoal. It

burns with little flame, but it has a high heat content. Hence it finds use as a fuel. Coke is an *excellent reducing agent*. For

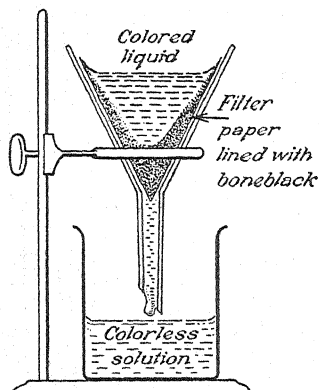


FIG. 148. — Some liquids are decolorized by filtering them through lampblack.

every pound of iron produced, it takes about one pound of coke. Many of the ores of iron, copper, tin, and zinc are oxides. To take the oxygen away from the metals in such ores, *millions of tons of coke* are used annually in the United States alone.

**228. Animal Charcoal, or Boneblack.** When bones, blood, or animal refuse is heated in retorts, *animal charcoal*, or *boneblack* is left as a residue. *Bone oil* and *pyridine* are obtained as by-products from such destructive distillation. Bone-

black usually contains considerable mineral matter, present as calcium phosphate. Sometimes it is treated with an acid to dissolve the mineral matter.

Like charcoal, boneblack is also a good adsorbent. It finds use in decolorizing and clarifying liquids, especially crude sugar solutions. Figure 148 shows a diagram of a boneblack filter that may be used to remove the brown color from a solution of crude sugar.

**229. Lampblack.** Possibly at some time you may have lighted a kerosene oil heater, and turned the wick a little too high. You found that finely divided particles of carbon are set free when kerosene oil burns in an insufficient amount of air.

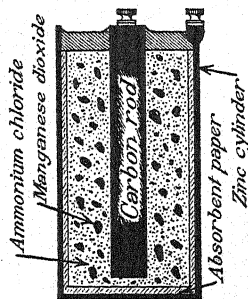


FIG. 149. — Gas carbon rods are used for making dry cells.



The *lampblack* of commerce is made by burning oils in an insufficient supply of air. *Carbon black*, made by burning natural gas in an insufficient supply of air, is not so greasy or tarry as lampblack. In commercial practice, the carbon is deposited on the cool under-surface of a revolving disc, and scraped off into bags.

Lampblack is a velvety powder, which finds use in making printer's ink, shoe polish, India inks, carbon paper, black varnishes, and as a pigment in paints. Used as a filler in automobile tires, it helps to conserve the life of the rubber.

**230. Gas Carbon.** In the manufacture of coal gas, finely divided carbon collects on the walls of the retorts. When it is collected and pressed into sticks, it becomes quite a good conductor of electricity. Gas carbon is used to make the positive plate of dry cells, and for making the rods for use in the electric arc. (See Fig. 149.)

### SUMMARY

Carbon is present in the air in the form of carbon dioxide; it occurs in all organic matter, both plant and animal. It is found uncombined in graphite and the diamond.

Carbon exists in three allotropic forms: *amorphous carbon*, *graphite*, and the *diamond*.

*Diamond*, a crystalline form of pure carbon, is the hardest mineral known. It finds use in jewelry, and as an abrasive.

*Graphite*, a soft, crystalline form of carbon, is used as a lubricant, in paints, as electrodes, for making crucibles, and in "lead" pencils.

*Artificial graphite*, *calcium carbide*, *carbon disulfide*, *carbon tetrachloride*, "*Carborundum*," and *high grade steels* are products of the electric furnace.

*Charcoal* is made by the destructive distillation of wood; *coke* is made by the destructive distillation of soft coal; and *boneblack* is made by the destructive distillation of bones.

At ordinary temperatures, all forms of carbon are inert; at higher temperatures, they unite with oxygen to form either carbon monoxide or carbon dioxide.

*Carbon adsorbs gases;* hence it is suitable for use as a deodorizer, a decolorizer, and for use in gas masks. Because it is insoluble in ordinary reagents, it is useful in pigments, in paints and lacquers, and in printer's ink.

### QUESTIONS

1. Why is it so difficult to remove stains made by printer's ink?
2. Why is carbon one of the most important elements?
3. What properties has graphite that make it useful for stove polishes?
4. Why is graphite suitable for use in paints?
5. What makes a kerosene lamp burn with a smoky flame?  
Suggest two remedies.
6. Make a list of products made in the electric furnace. Is it the electricity or the heat that causes the chemical reactions?
7. Why is the name "lead" pencil misleading? Suggest a better name.
8. Does charcoal decay? Why are posts sometimes charred before they are put into the ground?
9. How would you prove that the various allotropic forms of carbon contain nothing but carbon?
10. How would you distinguish diamonds from cut glass brilliants?
11. Which of the forms of carbon, if burned in oxygen, will give the lowest per cent of ash?
12. Powdered charcoal, copper oxide, and manganese dioxide all have the same appearance. How would you identify each one?
13. How would you proceed to show that a sample of sugar contains carbon?
14. Write equations to show two products that may be formed when charcoal burns in air.
15. Discuss the changes that a piece of charcoal may undergo in order to become a piece of protoplasm in your body.
16. Charcoal tablets are sometimes used medicinally. Explain why they relieve flatulency.



## CHAPTER 19

### TWO OXIDES OF CARBON

#### Vocabulary

**Fermentation.** A chemical change produced by some micro-organism, such as yeasts or bacteria.

**Sublime.** To change from a solid state to a vapor without liquefying.

**Dehydrate.** To remove water from a substance.

#### A. CARBON DIOXIDE

**231. Where Carbon Dioxide Is Found.** We know that carbon dioxide is found in the air at all times. It is constantly being given off by the breathing of animals, and as a product of ordinary combustion.

**232. How Carbon Dioxide Is Prepared.** Of the several methods of preparing carbon dioxide, three are given here:

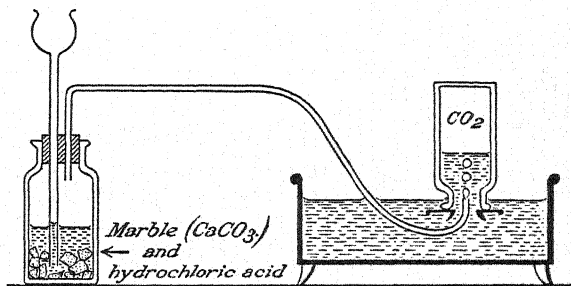
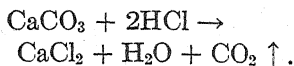


FIG. 150. — A carbon dioxide generator.

1. *By burning carbon.* This method has already been given. We know that carbon dioxide is one of the products of combustion whenever any material that contains carbon is burned. If we use this method of preparing the gas, it will

be contaminated with the constituents of the air and with other products of combustion.

2. *Action of acids on carbonates.* (Usual laboratory method.) If we pour a little hydrochloric acid on some lumps of marble, which is *calcium carbonate*,  $\text{CaCO}_3$ , carbon dioxide will be evolved and calcium chloride will be formed. (See Fig. 150.) The equation for the reaction follows:



It is probable that *carbonic acid*,  $\text{H}_2\text{CO}_3$ , is first formed, and that it decomposes, liberating the gas, which bubbles off with effervescence. (See Fig. 151.) The gas may be collected by water displacement, if it is generated rather rapidly. It may also be collected by air displacement.

FIG. 151. — Carbon dioxide escapes with effervescence when an acid is added to a carbonate.

carbonate. For example, sodium carbonate reacts with sulfuric acid and liberates carbon dioxide. The action of an acid on a carbonate with the liberation of carbon dioxide with effervescence is so typical that it serves as a *test for carbonates*. An equation follows:

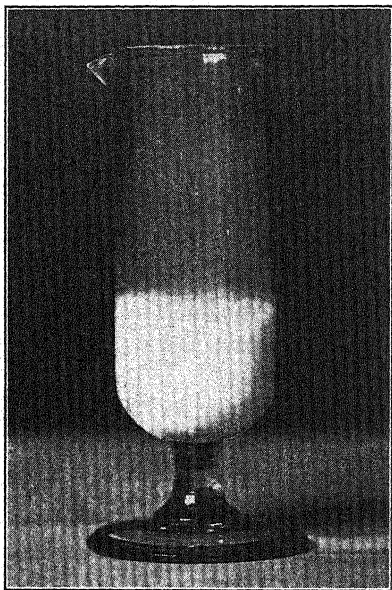
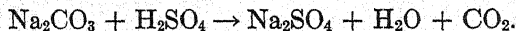


Photo by Wetlin

3. *By heating carbonates.* (A commercial method.) In the manufacture of quicklime,  $\text{CaO}$ , limestone is strongly heated. Limestone is also a form of calcium carbonate; it gives up its carbon dioxide when it is heated. The equation for the reaction follows:



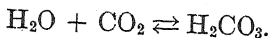
Nearly all carbonates behave in a similar manner when they are heated, although the carbonates of sodium and potassium are exceptions.

**233. Physical Properties of Carbon Dioxide.** This gas is colorless, but it has a slightly pungent odor and taste. It is about  $1\frac{1}{2}$  times as heavy as air. Hence it can be poured from one vessel to another. It usually diffuses with the air, but sometimes it collects at the bottom of dry wells, mines, and caves. Before entering a dry well, workmen often lower a lighted candle to see whether there is enough carbon dioxide present to extinguish the flame. If the candle goes out, the air is unfit to breathe, and the heavy gas must be bailed out with buckets before it is safe for the workmen to go down. It is amusing to see a man lower a bucket on a rope, raise it again, and pour out *apparently* nothing, a colorless gas. *Carbon dioxide is not poisonous*, but animals die in it from suffocation. The gas is easily liquefied, and the liquid carbon dioxide is sold in steel cylinders.

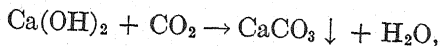
If a cloth bag is held over the mouth of a cylinder of liquid carbon dioxide, and the valve is opened, the cooling effect produced by the rapid evaporation of the liquid will cool some of the remaining liquid enough to form particles of carbon dioxide ice or snow.

**234. The Chemical Behavior of Carbon Dioxide.** This gas is very *stable*. It neither burns nor supports combustion, although burning magnesium is hot enough to decompose carbon dioxide, and continue to burn by taking the oxygen from it and leaving the carbon uncombined.

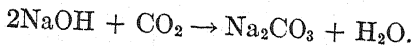
Carbon dioxide dissolves in *cold* water readily, or perhaps it is better to say it interacts with water. It is the *anhydride of carbonic acid*. This is a weak acid that exists in water solution only. It is easily decomposed by heat, as represented by the reversible equation:



When carbon dioxide is passed into the water solution of a base, it unites with the base to form a carbonate. This reaction we have already studied in the test for carbon dioxide by passing the gas into lime water, or calcium hydroxide. The equation,



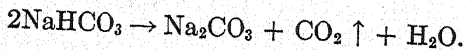
shows that calcium carbonate is precipitated. The reaction with other bases is similar, although some carbonates are soluble and no precipitate is formed. For example,



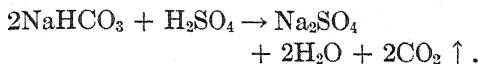
**235. The Uses of Carbon Dioxide.** This gas finds such wide and varied use that several companies manufacture liquid carbon dioxide for the market. It is also used in making the carbonates of sodium and in the manufacture of white lead; processes which are discussed elsewhere.

1. *As a plant food.* The carbon dioxide-oxygen cycle has already been discussed. Carbon dioxide from the air supplies plants with the carbon they need for making starch, oils, and proteins.

2. *In fire extinguishers.* Since carbon dioxide does not burn, it may be used to extinguish fires. Dry baking soda,  $\text{NaHCO}_3$ , decomposes when thrown on a fire, and sets free carbon dioxide, which blankets the fire and shuts off the oxygen supply.



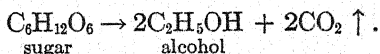
In a fire extinguisher of the type shown in Fig. 152, about  $1\frac{1}{2}$  lb. of baking soda are dissolved in water. The small, loosely stoppered bottle contains concentrated sulfuric acid. When the extinguisher is turned bottom side up, the acid spills out and mixes with the baking soda solution. The chemical reaction is represented by the equation,



The pressure of the gas forces a stream of water and carbon dioxide bubbles into the fire. The use of *firefoam* with extinguishers of this type is discussed in Section 416.

3. *In carbonated beverages.* Some mineral waters contain considerable quantities of carbon dioxide in solution. The soft drinks that are sold so extensively are charged by forcing carbon dioxide into the beverages under pressure. Effervescence occurs when the bottle is opened. Soda water is charged in the same manner by forcing carbon dioxide into the fountain under a pressure of several atmospheres. Some fermented beverages are charged with the carbon dioxide that is produced during fermentation.

4. *As a leavening agent.* In the baking of bread, yeast is used to act upon starches and sugars and cause fermentation, which may be represented by the following equation:



As the bubbles of carbon dioxide become entangled in the plastic dough, they cause it to rise, not only while they are

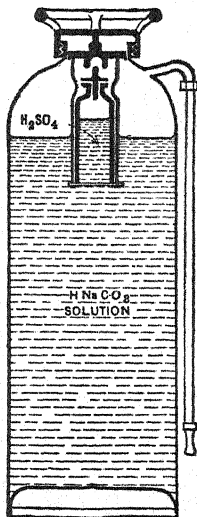


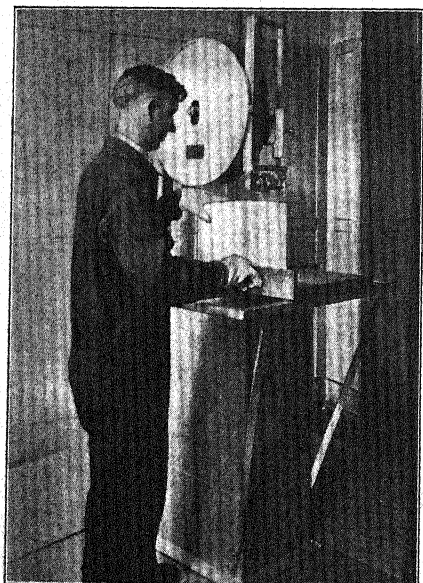
FIG. 152. — Carbon dioxide fire extinguisher.

being liberated, but also in the oven when they are heated during the baking (Law of Charles). In many large bakeries compressed air is used for leavening.

There are other ways of liberating carbon dioxide without the use of yeast. Sour milk contains an acid which interacts with baking soda and liberates carbon dioxide. Molasses

unites chemically with baking soda and sets free the carbon dioxide.

Baking powders differ from baking soda, because they contain the soda and some acid substance mixed with it. Starch is used to keep the powder dry, and the soda furnishes the carbon dioxide. The acid compound varies with the type of baking powder. Some powders contain cream of tartar or tartaric acid; another type uses calcium acid phosphate;



*Courtesy "Dry Ice" Corporation*

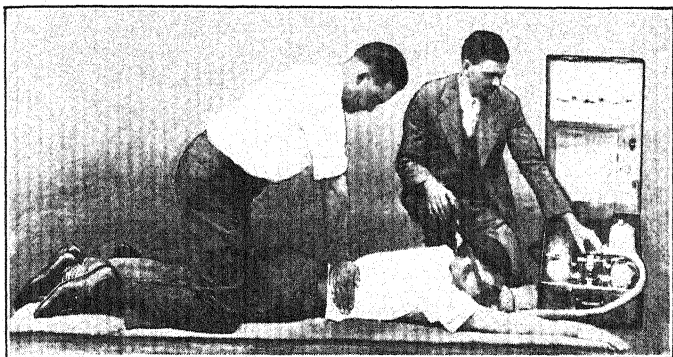
FIG. 153. — Solid carbon dioxide may be sawed into blocks.

and a third type uses a double salt, anhydrous sodium aluminum sulfate.

5. *As a refrigerant.* In Section 233 we learned that solid carbon dioxide may be formed by the rapid evaporation of liquid carbon dioxide. This solid has a temperature almost 80 below zero Centigrade. In a proper container, 1 pound of it is as effective a cooling agent as from 10 to 15 pounds of

ice. It does not wet material with which it comes into contact, because it *sublimes*, or changes from the solid to the gaseous state, without melting. (See Fig. 153.) It is commercially manufactured under the name of "dry ice."

For shipping foods it is quite useful. *Its temperature is so low that it must not be handled with bare hands, as it produces such serious freezing that amputation may be necessary.*



Courtesy of Mine Safety Appliances Co.

FIG. 154. — A mixture of carbon dioxide and oxygen, called carbogen, is used for resuscitation work.

An interesting experiment in rain-making was tried successfully over the Zuyder Zee in Holland. Finely divided solid particles of carbon dioxide were sprayed from an airplane at a high elevation. Such sudden chilling of the air caused the moisture of the air to condense and form rain.

6. *In resuscitation work.* It seems strange to think of using carbon dioxide for pneumonia and asphyxiation from poisonous gases, but a few per cent of carbon dioxide will accelerate respiration. A mixture of from 5% to 10% of carbon dioxide with pure oxygen, known as *carbogen*, is often used. Hospitals use such a mixture in treating alcoholic poisoning. The oxidation of the alcohol increases the amount of carbon dioxide and lactic acid in the body. The carbon

dioxide of the carbogen mixture increases the respiration rate and the oxygen completes the oxidation of the lactic acid which causes the "hang over."

### B. CARBON MONOXIDE

**236. Introductory.** Every few days we read in the newspapers that someone has lost his life by inhaling this

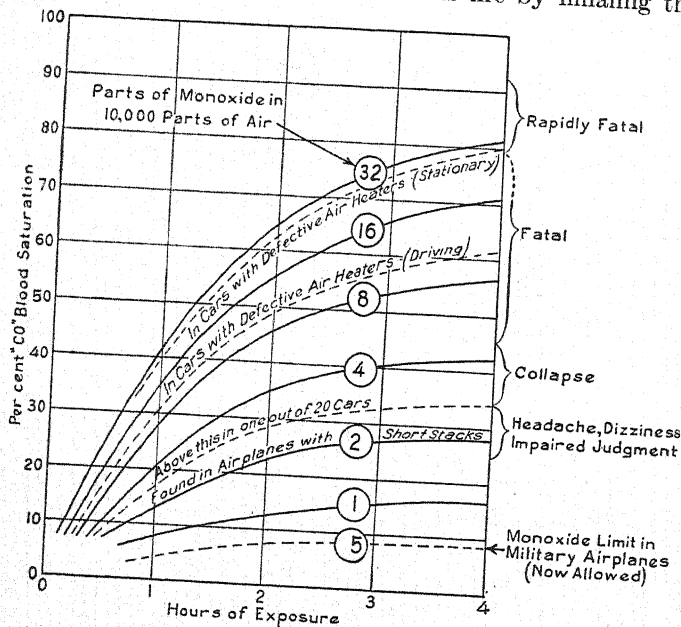


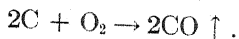
FIG. 155. — The graph shows the effect of inhaling carbon monoxide.

*Courtesy of Scientific American*

treacherous gas, carbon monoxide, CO. It may be that the gas escaped from a fire that was improperly banked, or possibly someone left his engine running in a closed garage. Even a small car will set free enough of this gas in five minutes to make the air in a closed garage dangerous.

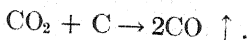


**237. How Carbon Monoxide Is Prepared.** 1. *When carbon burns in an insufficient supply of air.* When carbon burns in air or oxygen, carbon dioxide is formed. But if there is not enough air or oxygen present to combine with all the carbon, then the following reaction occurs:



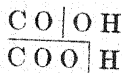
The gas is usually mixed with other gases when a fuel burns without having a proper draft. This source of carbon monoxide is a rather dangerous one, as it is usually the result of improperly banked fires.

2. *From the reduction of carbon dioxide.* When carbon dioxide comes into contact with white-hot carbon or coal, it is reduced to carbon monoxide. This reaction is an important one, because carbon monoxide is very useful in the extraction of metals from their ores.



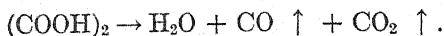
The carbon monoxide that is produced takes the oxygen from the hot ore and forms more carbon dioxide; the metal is left uncombined.

3. *From the decomposition of oxalic acid.* This is the usual laboratory method of preparing carbon monoxide. All organic acids have one or more COOH groups in their composition. Oxalic acid is made up of two such groups. It has the formula  $(COOH)_2$ . When this acid is heated with sulfuric acid, which is a good *dehydrating* agent, one molecule of water is abstracted from a molecule of the oxalic acid by the sulfuric, and the rest of the oxalic acid molecule then decomposes into carbon monoxide and carbon dioxide. The following formula shows how the molecule is decomposed:



When the  $H_2O$  is taken away by the sulfuric acid, the rest of the molecule splits into two parts as indicated by the lines.

The carbon dioxide may be separated from the carbon monoxide by bubbling the gases through sodium hydroxide solution. The carbon dioxide unites with the sodium hydroxide and forms sodium carbonate, but the carbon monoxide is not dissolved. The equation for the decomposition of oxalic acid is as follows:



Since the sulfuric acid is not changed during the reaction, it is not included in writing the equation. The carbon monoxide is collected by water displacement. *The fact that this gas has no odor and that it is so poisonous makes its laboratory preparation by students ill-advised.*

**238. Physical Properties of Carbon Monoxide.** A colorless, odorless, tasteless gas, carbon monoxide is slightly lighter than air. Its density is the same as that of nitrogen. It is a difficult gas to liquefy. Carbon monoxide is only slightly soluble in water.

**239. Chemical Behavior of Carbon Monoxide.** Anyone who has watched the flame from a hard-coal stove has noticed the pretty, blue flame that is produced after a fresh supply of coal has been added. This is the flame from burning carbon monoxide. The burning gas from hard coal consists largely of carbon monoxide. It readily combines with oxygen, taking it from many other substances, and thus acting as a *reducing agent*.

As small an amount as 0.1 of 1% is dangerous to life, and rapidly produces fatal results. It is especially treacherous, since persons have no warning of its presence. In the few cases where persons who have been overcome by this gas have been resuscitated, they have stated that they did not realize they were in a dangerous atmosphere until they were unable to help themselves. Canary birds and white mice are very susceptible to this poison, and they are used in tunnels and mines to serve as a warning to the workers. It

combines with the hemoglobin in the red blood cells and makes them incapable of carrying oxygen. The compound it forms is so stable that artificial respiration is not very successful. In bad cases, blood transfusion is necessary.

Since the exhaust from motor vehicles contaminates the air quickly, *an engine should never be warmed up in a garage*. One of the big problems for the engineers constructing the Holland Tunnel under the Hudson River was that of adequate ventilation. In each of two ventilating buildings at the opposite ends of the 9250 ft. tunnel, there are 21 large electric fans, capable of forcing 1,900,000 cu. ft. of air per minute through the tunnel. There is no horizontal draft, but the air rises to the exhaust ducts directly.

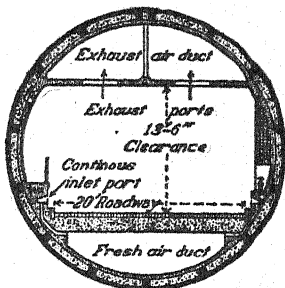


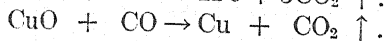
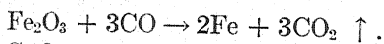
FIG. 156. — Cross-section of the Holland Tunnel.

(See Fig. 156.) Although millions of cars have passed through this tunnel, yet the ventilation has been successful.

**240. Uses for Carbon Monoxide.** There are three very important uses for carbon monoxide: (1) *As a reducing agent*; (2) *As a fuel*; (3) *For making wood alcohol*. During the war it was combined with chlorine in the presence of charcoal as a catalyst to make a very deadly gas known as *phosgene*,  $\text{COCl}_2$ . It is suffocating; it attacks the membranes of the respiratory organs and tends to stop the action of the heart. Phosgene in 1700-lb. cylinders was being shipped from Edgewood, Maryland, to the shell-filling stations in France when the war ended in 1918. *Hopcalite*, a mixture of several metallic oxides, was used in gas masks to oxidize carbon monoxide and convert it into carbon dioxide.

1. *As a reducing agent.* In extracting iron, copper, zinc, and some other metals from their ores, carbon monoxide is used to take away the oxygen from the oxides of these metals.

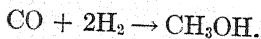
The carbon monoxide is obtained by the partial oxidation of coke, charcoal, or coal. The equations follow:



These reactions are typical of some of the most important ones in industrial chemistry, since they are used in obtaining our useful, heavy metals.

2. *As a fuel.* Sometimes when coal is burned, the carbon monoxide escapes up the chimney unburned. Then more than half of the fuel value of the coal is lost by incomplete combustion. Table 8, in the Appendix, shows us that more than 3 times as much heat is produced when 12 grams of carbon burn completely and form carbon dioxide, as are formed when 12 grams of carbon form carbon monoxide during partial combustion. Therefore, *incomplete combustion* forms a poisonous gas and wastes fuel badly. Many of the fuel gases discussed in the following chapter contain carbon monoxide.

3. *For making wood alcohol, or methanol.* The French and the Germans developed in 1924 a process for making wood alcohol from carbon monoxide and hydrogen. Under pressure the gases combine in the presence of a mixture of zinc oxide and copper used as a catalyst. The equation follows:



This process, now used extensively in the United States, is so efficient that it costs less to make methanol synthetically than it does by the old process of wood distillation.

### C. COMPOUNDS OF CARBON WITH NITROGEN

★ 241. **Cyanogen,  $\text{C}_2\text{N}_2$ .** This gas may be obtained by heating cyanides, such as mercuric cyanide,  $\text{Hg}(\text{CN})_2$ . It is a colorless gas that burns with a blue flame. Its odor is like that of peach leaves. This gas is exceedingly poisonous.

★ 242. **Hydrocyanic Acid and the Cyanides.** If a compound containing the cyanide radical ( $\text{CN}^-$ ) is treated with an acid, *hydrogen cyanide* ( $\text{HCN}$ ) is set free. It is a volatile liquid, boiling at  $26^\circ \text{C}$ ., just a trifle above room temperature. The water solution of hydrogen cyanide is called *prussic acid*, or *hydrocyanic acid*. The vapor of this acid has an odor similar to that of peach blossoms. It is one of the most poisonous substances known. It is used to destroy rodents and all forms of insect life on ships. Imported trees, shrubbery, and plants are often treated with the vapor of this acid to prevent the introduction of insect pests.

The most important salts of this acid are the *cyanides of sodium and potassium*,  $\text{NaCN}$  and  $\text{KCN}$ . The *cyanide radical*, ( $\text{CN}$ ), has a valence of 1. Large quantities of sodium cyanide are used in silver-plating baths, and in the extraction of gold from its ores by the cyanide process. The cyanides also find use in one of the special treatments for hardening the surface of steel, in destroying rodents, and as insecticides. With perhaps one exception, compounds containing the cyanide radical or group are extremely poisonous.

**CAUTION:** *Some cough syrups contain hydrocyanic acid; their excessive use may be dangerous.*

## SUMMARY

*Carbon dioxide* gets into the air by ordinary combustion and by the breathing of animals. It may be prepared by the *combustion* of carbonaceous material, by *heating a carbonate*, or by the *action of an acid on a carbonate*.

Carbon dioxide is a heavy, colorless gas, moderately soluble in water. Its water solution is known as *carbonic acid*. Carbon dioxide is stable. It does not burn, neither does it support ordinary combustion.

Carbon dioxide has several important uses: (1) *it is used by plants during photosynthesis*; (2) *in fire extinguishers*; (3) *as a leavening agent*; (4) *in carbonated beverages*; (5) *as "dry ice."*

Carbon monoxide is prepared: (1) *when carbon dioxide is reduced by carbon*; (2) *by the incomplete combustion of carbon*; (3) *by heating oxalic acid with concentrated sulfuric acid*.

Carbon monoxide is a colorless, odorless, tasteless gas; it is very poisonous. It burns with a blue flame, and it is an excellent *reducing agent*.

Carbon monoxide is used as a fuel and as a reducing agent. During the war it was used in making phosgene. It is not adsorbed by charcoal in gas masks, but it may be oxidized to carbon dioxide by the use of a mixture of oxides known as "Hopcalite." Large quantities are used in making wood alcohol, or *methanol*.

Cyanogen is a compound of carbon and nitrogen. It is very poisonous. Hydrogen cyanide,  $\text{HCN}$ , dissolves in water to form a poisonous liquid known as hydrocyanic acid, or prussic acid. The sodium salt of this acid finds use in electro-plating, in gold extraction, and in heat treatment of steel.

## QUESTIONS

### GROUP A

1. Why might a block in traffic in the vehicular tunnel under the Hudson River become dangerous?
2. How would you distinguish carbon dioxide from nitrogen? Carbon monoxide from hydrogen? Nitrous oxide from oxygen?
3. Devise a satisfactory test for a carbonate.
4. Name three reducing agents that we have studied.
5. Name at least five oxidizing agents that we have studied.
6. In parallel columns compare the properties of carbon monoxide with those of carbon dioxide.
7. What ingredient is present in nearly all baking powders? What is its purpose? Why is sour milk used with soda in baking?
8. What is meant by a dehydrating agent?
9. What are the physiological effects of carbon monoxide? Why is artificial respiration of little use when one is overcome with carbon monoxide?
10. Make a list of all the cases you can where one might be exposed to danger from carbon monoxide poisoning.

11. How would you proceed to prove that carbon dioxide is considerably heavier than air?

12. What objection is there to running an automobile engine in a garage in the winter time to warm the engine or the garage?

## GROUP B

13. A stick of sodium hydroxide changes to a white powder when exposed to air. Write the equation for the reaction.

14. Is there any "soda" in "soda water"? Can you suggest a reason for the name?

15. Why is hydrochloric acid used in preference to sulfuric acid in preparing carbon dioxide from calcium carbonate?

16. When a bottle of lime water is left unstoppered, a white ring is formed on the bottle at the surface of the liquid. Explain. How can this ring be removed?

17. What gas would you expect to be liberated when formic acid,  $\text{HCOOH}$ , is warmed with sulfuric acid?

18. Since "dry ice" costs about 10 times as much as ordinary ice, how can it compete with ice?

19. The label on a sodium bicarbonate fire extinguisher reads "Tested at 350 lb. per sq. in. pressure." Explain.

20. It is claimed that tobacco smoke contains small quantities of carbon monoxide. If you must smoke, what precautions should be taken?

## PROBLEMS

## GROUP A

1. How many pounds of ferric oxide can be reduced by 20 lb. of carbon monoxide? (Equation, page 308.)

2. How many grams of carbon dioxide are formed when sulfuric acid dehydrates 100 gm. of oxalic acid?

## GROUP B

3. How many liters of carbon monoxide are set free in No. 2?

4. Calculate the weight of one liter of carbon monoxide. What is the weight of one liter of cyanogen?

5. Calculate the number of liters of carbon dioxide that can be obtained from 1.5 lb. (454 gm. each) of sodium bicarbonate.

## CHAPTER 20

### FUELS AND ILLUMINANTS

#### Vocabulary

**Calorimeter.** An instrument used to measure the heat content of a fuel.

**British Thermal Unit.** The amount of heat needed to warm 1 lb. of water 1° F.

**Hydrocarbon.** A compound containing hydrogen and carbon only.

**Cracking.** Referring especially to the splitting up of complex molecules into simpler molecules.

**Capillarity.** The rise of liquids in hair-like tubes, or tubes of small diameter.

#### A. FUELS

**243. What Is a Fuel?** If a substance burns and supplies heat and energy, it is really a fuel. Some of them are solid; several of them are liquid; and some are gaseous. They nearly all come directly from the plant kingdom, either from plants of the present time, or formed from plants that grew millions of years ago. Almost without exception, they are compounds of carbon.

**244. The Choice of a Fuel.** In selecting a fuel, one looks for certain desirable qualities, and attempts to avoid fuels that have objectionable qualities. The ideal fuel should be low in cost, it should be easily kindled, and it should have a high heat content. On the other hand, there should be little ash or refuse, and no waste products that may become a nuisance. Few fuels, if any, meet all these conditions. The cost of some may be high, or their cost of transportation excessive. All solid fuels leave some residue as the fuel burns.

Let us consider soft coal. It is easily kindled; it does not burn up so rapidly that one must keep stoking the fire continuously; it has a high heat content; the amount of ash is



not excessive, running from 5 to 10 per cent; the cost is not exorbitant; but it is difficult to burn it so that dense clouds of soot and smoke do not belch out of the chimneys, or smudge the draperies in the house.

Students who have not had physics may not know how the heat content of a fuel is determined. A sample of coal is powdered, dried, and weighed; then it is mixed with some oxidizing agent so it can be burned in a closed vessel, or bomb. The bomb is surrounded with a known weight of water whose temperature is carefully measured just before the experiment is begun. Electric wires dip into the bomb so the coal can be ignited. As the coal burns, the bomb is rotated to keep the water stirred so the heat will be absorbed

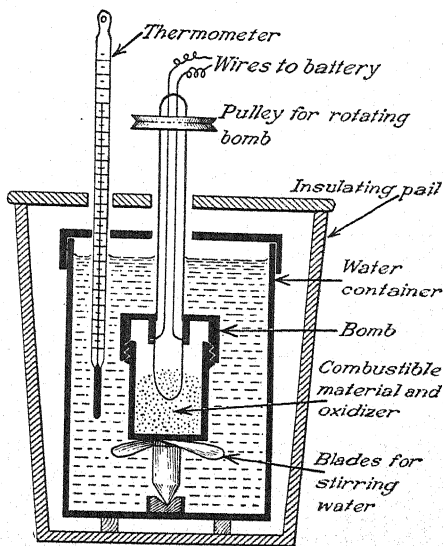


FIG. 157. — A bomb calorimeter by means of which fuel values can be determined.

by the entire mass of water. Figure 157 shows a type of bomb calorimeter used for determining the heat content of fuels. The increase in temperature of the water is noted.

We have already had the calorie defined as the amount of heat needed to warm 1 gm. of water  $1^{\circ}$  C. Knowing the weight of the coal, the weight of the water, and the number of degrees the water was warmed when the coal burned completely, it is a matter of simple arithmetic to calculate the number of calories 1 gm. of the fuel liberated. If the result is

wanted in Btu's, the temperature is taken in degrees Fahrenheit. One *British Thermal Unit* is the amount of heat needed to warm 1 lb. of water 1° F. The British Thermal Unit is abbreviated either B. T. U., or Btu. When a biologist says that a thick slice of bread furnishes 100 calories, he means that

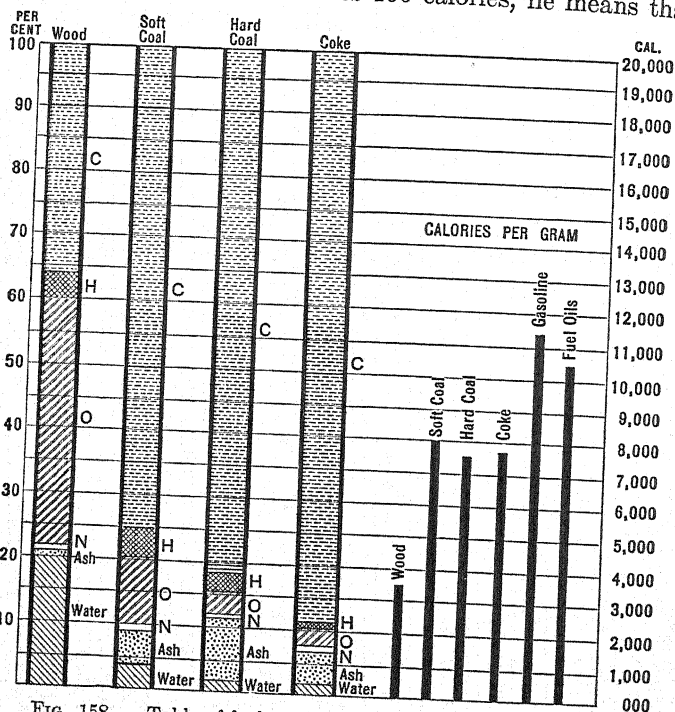


FIG. 158. — Table of fuel composition. Relative heat content of fuels.

such a slice of bread would, if burned in a bomb calorimeter, supply enough heat to warm 1 Kgm. (1000 gm.) of water 100° C. The *Calorie* as used in dietetics is 1000 times as large as the *calorie* used by the physicist.

**245. Of What Are Fuels Composed?** A glance at the accompanying table, Fig. 158, shows that nearly all fuels con-

tain large quantities of carbon, either free or combined. Many of them contain hydrocarbons, which are compounds containing hydrogen and carbon only. Wood, for example, contains considerable water, and the heat needed to evaporate such water must necessarily be subtracted from the fuel value. Oxygen in a fuel makes it burn with a cleaner flame, but since oxygen is not combustible, it does not add to the fuel value, and it increases the weight of the fuel. Wood, which has considerable moisture and also a high percentage of oxygen, has a low heat content compared to coal.

**246. What Products Are Formed By Burning Fuels?** If a fuel contains nothing but carbon, nothing but the oxides of carbon will be formed when it burns. If the fuel also contains hydrogen, water will be formed. Some hydrocarbons contain such a high per cent of carbon that it is difficult to bring into contact with them enough oxygen to burn the hydrogen and all the carbon. In such cases, the products of combustion may be water, some carbon dioxide, and some carbon monoxide. In some cases dense clouds of unburned carbon escape into the air. Such combustion not only pollutes the air, but it wastes tremendous quantities of fuel. Table 8 in the Appendix shows that we get 97,000 calories by burning 12 gm. of carbon to carbon dioxide, and that we get only 29,000 calories when 12 gm. of carbon are burned to carbon monoxide.

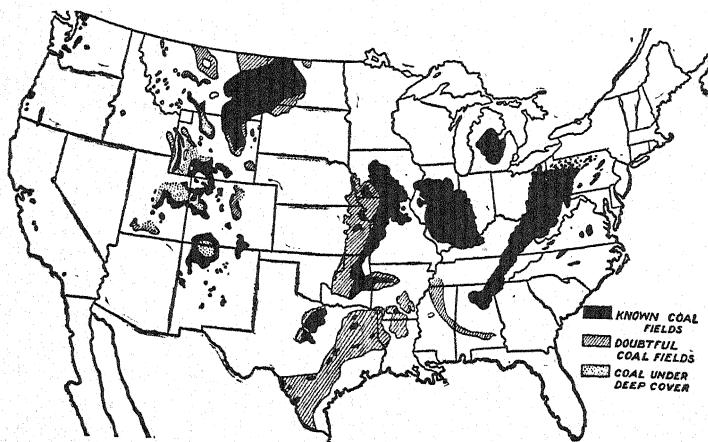
## B. SOLID FUELS

**247. Wood.** Probably no fuel is more widely distributed than wood. In localities where its cost is not great, it meets all the demands for a good fuel, except that its heat content is not very high. Even in localities where other fuels are used, wood is used for kindling and in fireplaces because an open wood fire in a room is an aid to cheerfulness.

**248. Peat.** The first step in the evolution of coal is peat. It is formed from club mosses and other forms of vegetation

by their partial decomposition in bogs or marshes. When dried, it burns with a smoky flame. It is not a very satisfactory fuel.

**249. Lignite.** In past geologic ages, several millions of years ago, vegetation on the earth was much more luxuriant than now. Tree ferns, giant club mosses, and other forms of vegetation supplied the material for our coal deposits. The



Courtesy U.S. Geologic Survey

FIG. 159. — Map showing general distribution of coal fields in the United States.

various forms of coal seem to depend upon the temperature and pressure to which this vegetable matter was subjected after upheavals of the earth's crust had buried it beneath the surface. An early stage seems to have produced *lignite*, which is common in our western states. It burns with a smoky flame, and it is inferior to soft coal in its heating capacity. It disintegrates badly when it is stored.

**250. Soft, or Bituminous Coal.** The great majority of the states in the United States contain beds of this fuel. (See Fig. 159.) It contains a larger percentage of carbon than

lignite does, and has higher heat content. While its origin from vegetable matter is not so clearly shown as in the case of lignite, yet many samples are found that prove that coal is really a fossil form of prehistoric plants. It is the most extensively used fuel for heat and power purposes.

**251. Hard Coal, or Anthracite.** The State of Pennsylvania has a near-monopoly on hard coal in the United States. Hard coal contains more carbon than soft coal, and less volatile matter. The percentage of ash is likely to be high. It has a high heat content, and it burns with a clean flame. For localities not too far distant from Pennsylvania, it makes a highly satisfactory fuel. In its process of formation, it was no doubt subjected to a high temperature and to great pressure. Practically all trace of its vegetable origin has been obscured.

**252. Coke.** The residue left after the destructive distillation of coal, or the fractional distillation of petroleum, is called coke. The petroleum coke is especially satisfactory as a fuel, but it is difficult to obtain, since the demand is greater than the supply. Coke burns with a clean flame, and makes a good fuel.

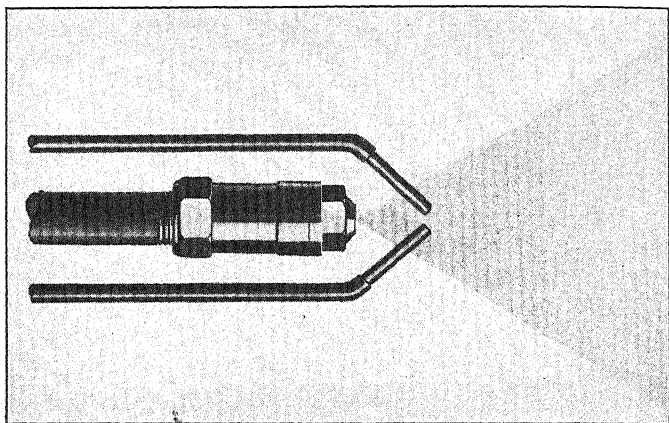
### C. LIQUID FUELS

**253. Source of Liquid Fuels.** Most liquid fuels, too, are of plant origin. The petroleum deposits may have been formed from certain carbides, but it is also possible that the carbon for these carbides came originally from plants. The alcohols are also for the most part of plant or vegetable origin.

**254. The Alcohols.** The compounds of this group resemble the bases in some respects. They all contain one or more hydroxyl, OH, groups, united with a radical. For example, wood alcohol, or *methanol*, has the formula  $\text{CH}_3\text{OH}$ . Grain alcohol, or *ethanol*, has the formula  $\text{C}_2\text{H}_5\text{OH}$ . The alcohols all burn with a clean, hot flame. Their use for heating purposes is limited. "Canned heat" consists of a colloidal jelly of alcohol and stearic acid.

**255. Gasoline.** Millions of gallons of gasoline find use as a fuel in the so-called gas engines. The gasoline vapor explodes violently when mixed with air, and the force of such explosion is used to drive automobiles. *Benzol*, a coal-tar product, is about the only other motor fuel that finds any use whatever.

**256. Kerosene.** Another product obtained from crude oil is *kerosene*. It serves as a fuel, chiefly for cooking, in territories that do not have the advantages of either natural or



*Courtesy of May Oil Burner Corp.*

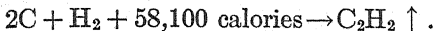
FIG. 160. — The oil is atomized before ignition to insure more complete combustion.

artificial gas. Its heat content is high, and in the right kind of a burner it burns with a clean flame. Its odor is unpleasant.

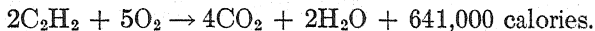
**257. Fuel Oils.** After the gasoline, kerosene, lubricating oils, and some other valuable products have been removed from petroleum by fractional distillation, certain hydrocarbons that are not particularly suited for other purposes are obtained as *fuel oil*. The improvement of burners and devices to atomize the oil has made it possible to burn such oil for heating houses or for factory use. (See Fig. 160.) The heat content is high, usually more than 10,000 calories per

are now in use. The powdered carbide is dropped into the water just fast enough to secure a steady evolution of the gas.

In the making of acetylene, heat is absorbed. The reaction is endothermic, as represented by the thermal equation:



When 2 moles of acetylene are burned we get all the heat that would be set free by burning an equal weight of free carbon (48 gm.) plus the heat that would be liberated by burning an equal weight of hydrogen (4 gm.) *plus* all the heat that was absorbed in making the acetylene.



With the exception of the atomic hydrogen flame, no flame is so hot. The temperature is estimated at from 3000° C. to 3700° C. Such a flame may be used for welding iron, as shown in Fig. 166. It is extensively used in the industries for such purposes. The tip of the flame is so hot that it may be passed over steel or iron plates many inches thick, and it will melt and burn the material in its path. Figure 167 shows a piece of steel over 10 in. thick that was cut by means of such an oxy-acetylene flame.

★ 265. **How Acetylene Is Stored.** Since heat is absorbed during the making of acetylene, the gas may explode without air or oxygen. Many dangerous explosions occurred when attempts were made to compress it in cylinders for shipment. The *prest-o-lite* container, in which acetylene may be safely stored, was developed about the time some were ready to discard the gas as a commercial product. (See Fig. 168.) This container is filled with asbestos soaked with acetone,  $(CH_3)_2CO$ , a liquid obtained from the destructive distillation

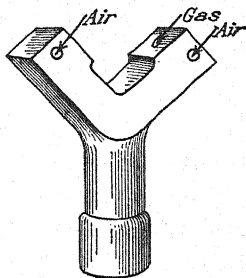


FIG. 165. — Acetylene burner.



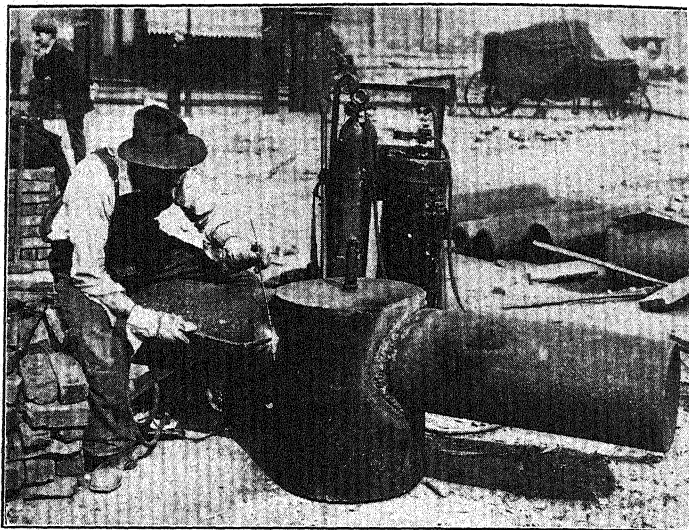


FIG. 166. — Welding with oxy-acetylene blowpipe. A completed weld shown at the right.

of wood. The acetylene will dissolve in the acetone under pressure. It escapes when the valve is opened and the pressure is removed.

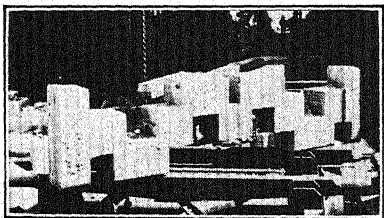


FIG. 167. — Crankshaft roughed out by the use of the oxy-acetylene flame.

★ 266. **Acetylene Beacons.** During the past 20 years, the use of acetylene for signaling devices has increased greatly. About 75% of the lighthouses use acetylene to flash warning signals. Every three

miles along the air-mail routes acetylene beacons have been placed to guide aviators. Hundreds of "silent policemen" are found at street intersections, at railroad crossings, and at the approach to dangerous curves and blind roads.



Dalen, a Swedish inventor, was awarded the Nobel prize in physics in 1912 for his work as inventor of the regulating devices which make the intermittent flashing of acetylene beacons automatic. Lighthouses in the Arctic regions operate without attention for as long as two years. A sun valve shuts off the gas when the sun shines, but it comes on again auto-

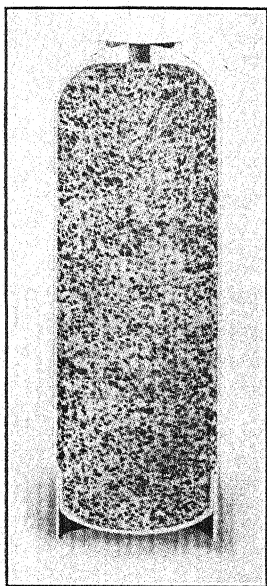


FIG. 168. — Cylinder for storing acetylene.

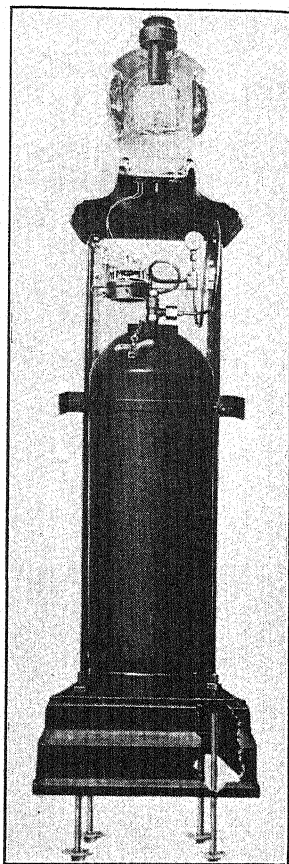


FIG. 169. — The inside mechanism of a "traffic beacon."

matically when it grows dark. A Welsbach mantle, used with such lights, is automatically replaced if accidentally broken. At about the time that Dalen completed these

inventions, an explosion cost him his eyesight. It seems a pathetic case that one man should give his sight that others may see.

In the traffic beacon, shown in Fig. 169, enough acetylene is stored in a strong, steel cylinder to last about six months. The gas flows out through a reducing valve that lowers its pressure to about  $\frac{3}{4}$  lb. per sq. in. The flow of the gas from this valve to the burner is controlled by a permanent magnet which lifts under pressure to let the gas escape. A pilot light at the base of the burner ignites the escaping gas and produces the intermittent flash.

**267. Explosion of Gases and Explosive Range.** We know that a mixture of hydrogen and oxygen explodes violently when ignited. Water gas, coal gas, or any other flammable gas, when mixed with air or oxygen, explodes when heated to its kindling temperature. The combustion is practically instantaneous throughout the entire mass. Gasoline, ether, and alcohol, in the liquid state, do not explode. But if they are converted into vapor, and the vapor is mixed with air, and then kindled, they explode with great violence. One pound of gasoline vapor, if mixed with exactly the right amount of air, is many times as powerful when exploded as the same weight of dynamite. In any mixture of gas and air, the explosion is most powerful when the gases are mixed in the ratio of their combining volumes. From Section 264, we conclude that acetylene will explode most violently when 2 volumes of acetylene are mixed with 5 volumes of oxygen, or about 25 volumes of air.

Fortunately, not all proportions of gas and air form explosive mixtures. A small per cent of illuminating gas does not explode when mixed with a large volume of air. The carburetor of a gas engine is designed to mix the gasoline vapor and air in just the right proportions to form the most powerful explosion possible. When the engine is cold, the gasoline does not evaporate fast enough and the mixture is "too lean"

to explode readily. When one pulls out the "choke," he cuts off some of the air supply and makes a "richer mixture." If the "choke" is pulled out too far, the cylinders may be "flooded" and then no explosion can take place. That means that the mixture of gasoline vapor is so rich that there is not enough air mixed with it to make it explode and start the engine. Any mixture of acetylene and air containing from 3% to 30% acetylene will explode. That *variation in percentage* is called the *explosive range* of acetylene. Any mixture of acetylene and air containing less than 3% of acetylene will not ignite; any mixture containing from 3% to 30% burns explosively; any mixture containing more than 30% burns quietly. Hydrogen has a wide explosive range, from 10% to 66%. The explosion is most violent when the mixture contains 29% of hydrogen. The following table shows the composition of some of the fuel gases.

ANALYSIS OF GASES (C. D. JENKINS, MASS. STATE REPORTS)

	Coal gas	Water gas (enriched)	Water gas	Oil gas
Candle-power .....	17.5	25	....	65
Illuminants .....	5	16.6	....	45
Marsh gas .....	34.5	19.8	1.0	38.8
Hydrogen .....	49	32.1	52	14.6 Ethane
Carbon monoxide .....	7.2	26.1	38	.....
Nitrogen and carbon dioxide	4.3	5.4	9.0	1.1

For determining candle-power 5 cu. ft. of gas are burned per hour.

### E. FLAMES AND ILLUMINANTS

**268. What Is a Flame?** We are all familiar with the flame produced when a gas is ignited. A candle burns with a yellow flame; but before this flame can be produced, the wax of the candle must be melted and then changed into a vapor. Let us take an Argand burner and place it over a

burning candle, allowing a little air to get in at the bottom, as shown in Fig. 170; we find that it is possible to extinguish

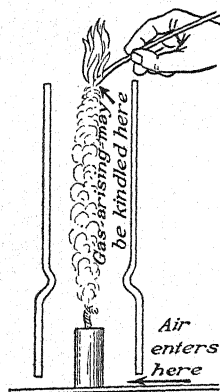


FIG. 170. — A flame is a burning gas.

the candle and then relight it by bringing a lighted taper just inside the top of the burner. The burning taper does not touch the wick, but it ignites the gas that is still escaping from it. This shows that a *flame is a burning gas*. A non-volatile substance does not burn with a flame. The volatile matter has been driven off in the preparation of coke and charcoal; hence these substances *merely glow* as they burn, but they produce little or no flame. For a similar

reason, hard coal produces little flame as it burns.

### 269. The Bunsen Burner.

When we depend entirely on the surrounding air to supply the oxygen needed to burn fuel gases, we find that some of the carbon escapes unburned. This wastes fuel, and deposits carbon on the utensils that are being heated. To avoid this, it is necessary to mix some air with the gas before it is ignited. In the burner shown in Fig. 171, which is one of the inventions of the German chemist,

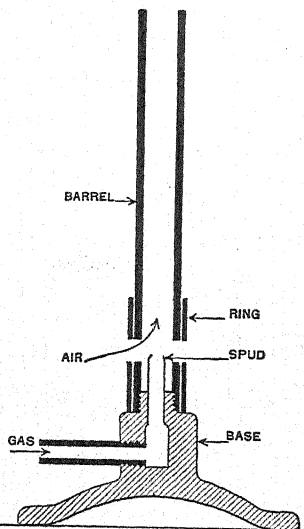


FIG. 171. — Parts of a Bunsen burner, longitudinal section.

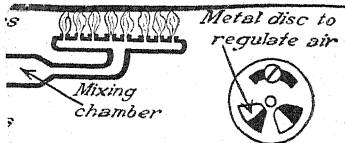
Robert Wilhelm Bunsen, the gas enters the tube or barrel through a small opening in the tip or spud. Air is drawn in through the holes at the lower end of the tube, and it mixes

with the gas in the tube before it reaches the top of the tube where it is ignited. (See Fig. 171.)

The amount of gas that enters the tube is regulated by the gas stop-cock. The ring is used to regulate the amount of air. By turning the ring, the holes in the bottom of the tube may be opened more widely, or even closed entirely. As more gas is used, more air should enter at the lower end of the tube. If the gas is partly turned off, or if the pressure is low, the holes must be partly closed to avoid forming an explosive mixture. When such a mixture is produced, the flame "strikes back" and burns at the spud. Poisonous gases are formed under such conditions, and both the tube and the base become hot. The rubber tubing may get hot enough to melt and cause a fire when the escaping gas becomes kindled. The gas should be shut off, and the burner properly regulated before it is relighted.

The flame of a Bunsen

burner consists of two distinct cones. (See Fig. 173.) The outer cone is called the oxidizing flame. A metal held in this flame of the burner will soon become *oxidized*. If the oxide of a metal, such as copper oxide, is held in the inner cone of the flame, it will be reduced to the metallic state. The inner cone is called the *reducing flame*. The zone just above the tip of the inner cone is the hottest part of the flame.



— The burner of a gas range is a modified Bunsen burner.

ars a great deal, and "strikes e, the holes should be closed t.

heating, we know that gas te in price with coal. For much more convenient, and paper. It has the following  
 (1) It is turned on only when  
 (2) It may be turned off imer the cooking is finished; e thing is being cooked, only d be used; (4) The heat may ed just where it is needed; is easily regulated.

andle Flame. The ordinary

**270. Luminous and Non-luminous Flames.** When the holes of the Bunsen burner are open the flame is nearly colorless and gives very little light. If we close the holes, a yellow luminous flame is produced. A beaker of cold water held in this flame is soon covered with soot, showing that the combustion of the carbon is incomplete. The light which a

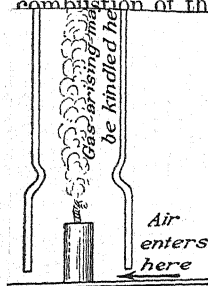


FIG. 170. — A flame is a burning gas.

gas that is in a kerosene lamp, or a gas shows that it gives is due to particles of unburned carbon which are heated with a flame incandescence. The flat flame has been driven by coke and stances in they produce little or no flame. For a similar

reason, hard coal produces little flame as it burns.

**269. The Bunsen Burner.** When we depend entirely on the surrounding air to supply the oxygen needed to burn fuel gases, and that some of the carbon escapes unburned. This waste of fuel, and deposits carbon on the

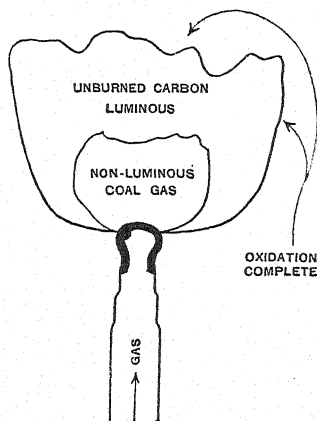


FIG. 174. — Gas jet, fish-tail burner.

portions that are being heated in which there are hot particles of carbon. (See Fig. 174.) This statement may be further verified by opening the holes to produce the hot, nearly colorless flame and then sprinkling particles of iron rust into the flame. The flame becomes luminous as the particles are heated white hot.

**271. The Gas Stove.** The ring burner, or the star-shaped burner used in gas stoves, does not differ in principle from the Bunsen burner. There are several small openings so the

flame will be distributed over a wider radius. In Fig. 175 we see that there is a mixing chamber and a ring of metal that can be used to regulate the amount of air that enters the mixing chamber. If the burner of your gas range gives a flame with yellow tips, it will waste fuel and also smoke up your kitchen utensils.

With a screw driver, you should loosen the set screw, turn the ring to increase the size of the air openings, and then tighten

the screw again. If the flame roars a great deal, and "strikes back" when it is lowered a little, the holes should be closed to some extent.

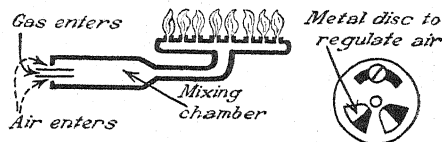


FIG. 175. — The burner of a gas range is really a modified Bunsen burner.

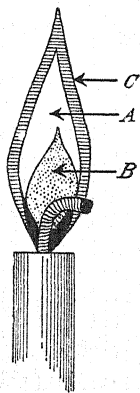


FIG. 176. — Candle flame, showing parts.

For general heating, we know that gas cannot compete in price with coal. For cooking it is much more convenient, and it may be cheaper. It has the following advantages: (1) It is turned on only when it is needed; (2) It may be turned off immediately after the cooking is finished; (3) If only one thing is being cooked, only one burner need be used; (4) The heat may be concentrated just where it is needed; (5) The heat is easily regulated.

**272. The Candle Flame.** The ordinary candle is made of paraffin, stearin, spermaceti, or other wax or fat. These substances all contain carbon and hydrogen. When they are heated, they melt, and the melted wax rises by capillarity to the end of the wick where it vaporizes and burns. Figure 176 shows that the flame has three distinct cones. Surrounding the wick is a cone of unburned gases. In the middle cone, the gases become hot enough to decompose some of the hy-



drocarbons, and some carbon is set free. As this carbon is heated to incandescence, it forms the luminous cone and becomes the light-giving area. In the outer, almost invisible, cone, the combustion is complete, and water and carbon dioxide are formed. In making the wicks of modern candles, one thread is drawn more tightly than the others. As the candle burns, the end of the wick is pulled to one side and burns in the edge of the flame. In this manner, the candle automatically trims itself.

★ 273. **Gas Mantles.** Electricity has rapidly replaced gas for illuminating

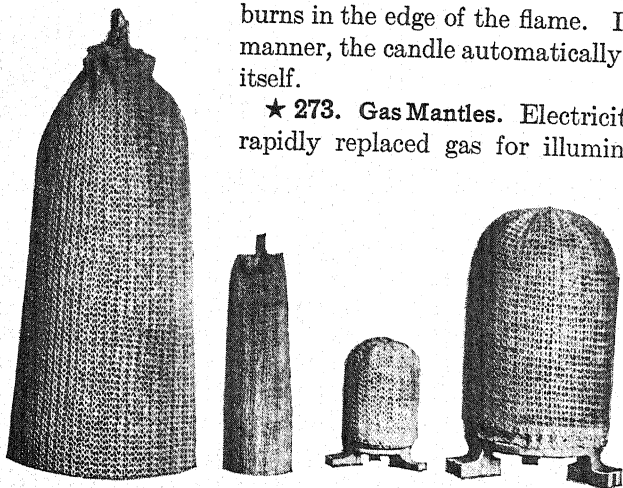


FIG. 177. — Welsbach gas mantles, erect and inverted types.

purposes, in spite of the fact that the gas mantle, devised by Dr. Auer von Welsbach, made it possible to utilize the heating effects of the gas flame. These mantles are made from artificial silk, which is dipped into solutions of the nitrates of cerium and thorium. When these nitrates are heated, the oxides are formed. They are heated to incandescence and thus increase the efficiency. (See Fig. 177.)

#### F. SMOKE AND SMOKE PREVENTION

274. **Combustion in Furnaces.** If we refer to Fig. 178, we may be better able to understand the chemistry of fuels and



combustion. In order to burn coal successfully, it must be placed on a grate so the air can be drawn in from underneath. In starting a fire, the draft should be open and also the damper in the furnace-pipe that leads to the chimney or flue. The coal is oxidized rapidly, and the waste products of combustion are swept up the chimney. But much of the heat is also carried away. To prevent such loss of heat energy, the draft should be closed after the fire gets a start, and the damper in the pipe should be nearly closed. Then just enough air will leak in around the draft to keep the fire burning. The *check draft* may be used to make the fire burn still more slowly; the cool air coming into the furnace at the top surface of the fuel cools the fuel until it may be only slightly above the kindling temperature. But it sweeps the hot gases up the chimney and *wastes fuel*. Throwing fresh coal on a fire cools it and slows down combustion for a time.

In a steam heater part of the water is vaporized, and the steam expands to fill the pipes and the radiators, where it loses heat to the rooms as it condenses.

Since coal is largely carbon, its combustion seems simple. If enough air is used, all the carbon will burn to form carbon dioxide. But when fresh fuel is added, the carbon of such fuel unites with the carbon dioxide coming from the live coals underneath, and carbon monoxide is formed:

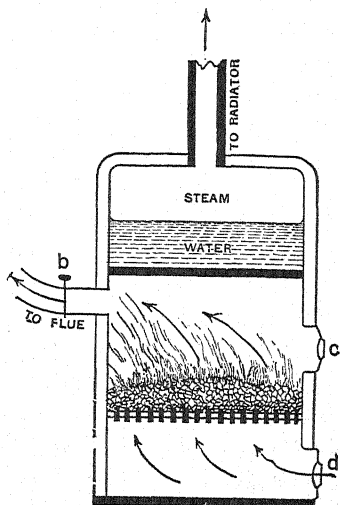
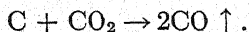


FIG. 178. — Steam heating furnace.

*The carbon is a reducing agent.* This gas may burn if there is enough oxygen; it may go up the chimney if the damper is open; it will go out and find its way to other parts of the house, if the furnace door is left open. In banking fires at night, *the furnace door should never be left open when the damper in the pipe is tightly closed.*

**275. Of What Does Smoke Consist?** Blue smoke from wood contains small drops of liquid hydrocarbons. Smoke from coal contains some finely divided ash, various gases, and some unburned carbon in the form of soot or cinders. In burning soft coal, it is difficult to supply enough oxygen to burn all the carbon. Hence in cities where large quantities of soft coal are used as a fuel or for power purposes, the smoke nuisance may become almost intolerable. It is estimated that the cost in the United States annually in wasted fuel, extra laundry work, and other expenses due to the smoke nuisance amounts to \$500,000,000. This cost does not include discomfort, or injury to health.

**276. Smoke Consumers.** We have learned that particles of unburned carbon in smoke are a menace to health, an expensive nuisance in many industries, and a decided waste in fuel energy. Every pound of carbon that escapes into the air in such manner represents a loss of from 10,000 to 15,000 Btu's. To eliminate the smoke nuisance, and to conserve this energy, many factories and power plants have installed *smoke consumers*. There are two things essential to smoke prevention: (1) The fuel must be supplied at a constant rate; (2) The supply of oxygen must be increased to secure *complete* combustion. Several types of automatic stoking devices are in use.

Figure 179 shows the plan of one type of stoker. From the hopper the coal is fed evenly to the moving chain grate just fast enough so the combustion will be complete by the time it reaches the far end of the grate. *Supplementary* air that has been *preheated* so it will not cool the flame is admitted

in order to oxidize the hydrocarbons completely before they reach the stack. Baffle walls are so built that the hot gases must take a circuitous path before they reach the chimney. This permits a more complete absorption of their heat energy, and allows more time for thorough combustion.

A rotating screw type of stoker is used on many locomotives. Mechanical stoking is necessary, when a large loco-

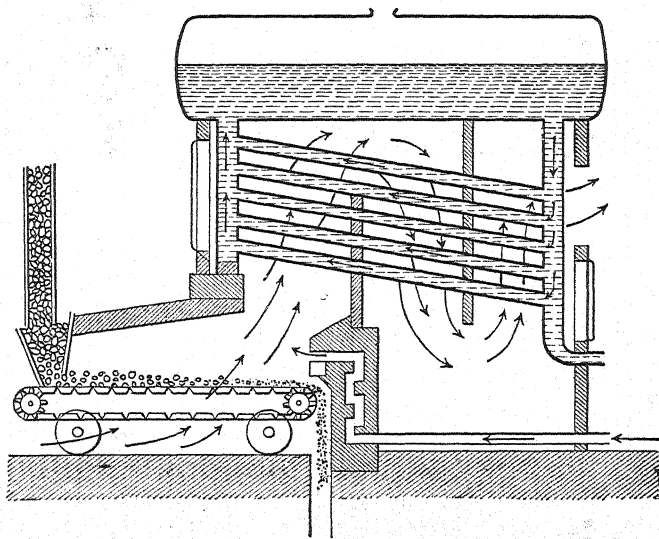


FIG. 179. — Automatic stoker and smoke consumer.

motive is burning from 4 to 6 tons of coal per hour. In the underfeed type of automatic stoker, the fuel is fed from a hopper to a feed trough that runs under the boiler the full length of the stoker. This trough becomes increasingly shallow, and the coal which is pushed backward overflows to the grates, to which air is supplied by a large blower or fan. Figures 180 and 181 show the effects of equipping the power plant of a factory with automatic stokers.

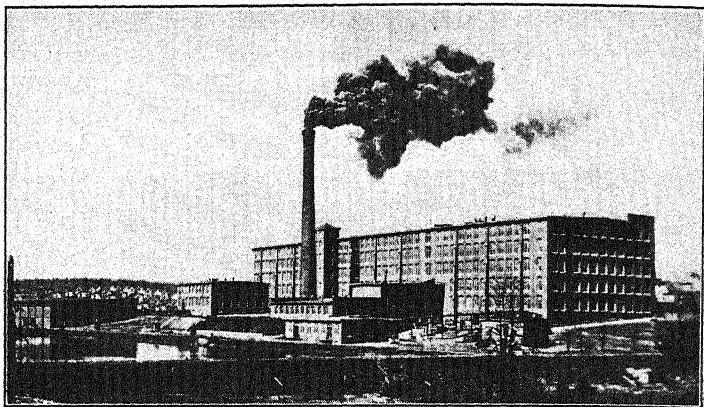


FIG. 180. — A factory that shows a dirty stack, illustrating the smoke nuisance.

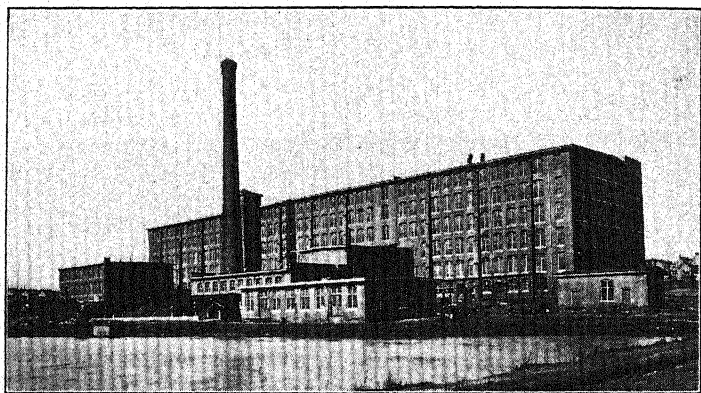


FIG. 181. — The factory shown in Fig. 180 after being equipped with an automatic stoker.

**277. Forced Draft.** Nearly every one has seen a blacksmith use a bellows to produce a *forced draft*. As he blows air through the glowing coals, he secures more rapid combustion for two reasons: (1) He is supplying a larger amount

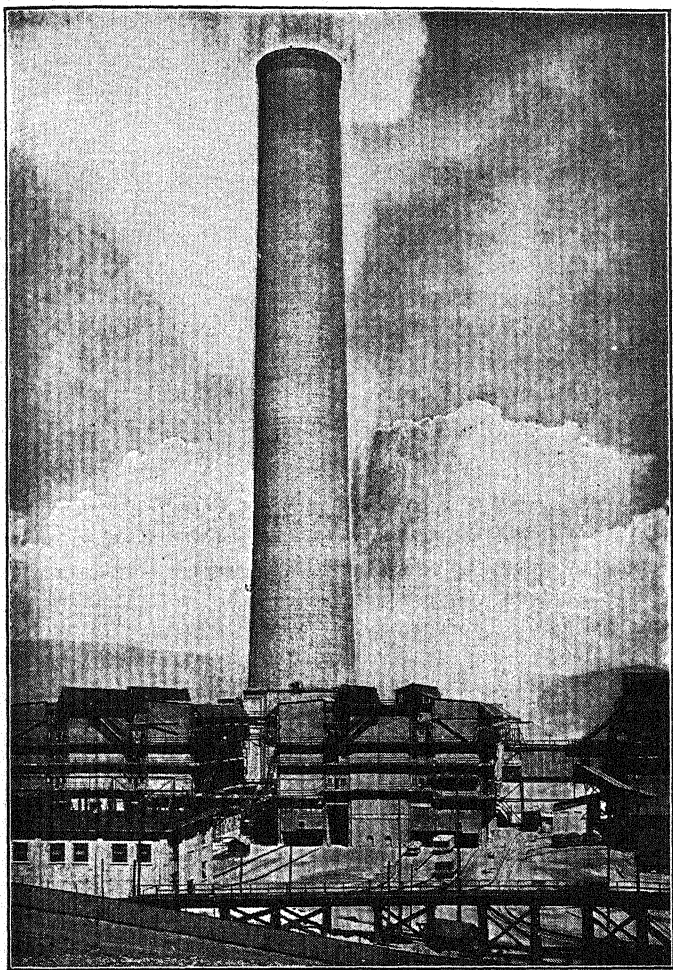


FIG. 182. — This stack built for smelting copper ores in Montana is so large that the Washington Monument would disappear from view if it were placed inside. Its height is 583 feet. Such stacks are usually equipped with electrical apparatus to precipitate the smelter dust and prevent it from escaping into the surrounding air.

of oxygen; (2) He is sweeping away the waste products of combustion. The more rapid burning increases the temperature. It is interesting to note that fuels burn faster and yield higher temperatures when both the fuel and the air with which it combines are *preheated*.

On ships, forced draft is used when a high speed is desired. More air is forced through the fuel, causing more rapid combustion. The exhaust steam from a locomotive is forced through the smokestack to produce a better draft. A similar effect is produced in power plants by using very tall chimneys. Since the draft of a chimney is caused by the difference in weight between the column of gas inside the chimney and the air-column outside, it is easy to see that this difference becomes greater as the height of the chimney is increased. (See Fig. 182.)

### SUMMARY

A substance that combines with oxygen to furnish heat energy is a *fuel*. A good fuel should yield little ash; it should be inexpensive; it should not produce undesirable waste products as it burns; and it should have a high heat content. Its heat content is determined by the use of a *bomb calorimeter*.

All fuels contain carbon and hydrogen, and many of them contain oxygen. Hence the products of combustion are water and carbon dioxide. Incomplete combustion produces carbon monoxide.

The *solid fuels* include: wood; peat; lignite; soft coal; hard coal; and coke. They are all obtained from plants, either those of the present time, or the fossil remains of plants that lived in past geologic ages.

The *liquid fuels* are also of plant origin. They include: the alcohols; gasoline; benzol; kerosene; and fuel oils.

Our most convenient fuels are the *gases*. *Natural gas* is found in many states. *Coal gas* is made by the destructive distillation of soft coal; ammonia, coal tar, and coke are valuable by-products. *Producer gas* is made by forcing a blast of hot air through a bed of coke. *Water gas* is made by forcing first a blast of hot air

through coke, and then a blast of steam. It is composed almost entirely of hydrogen and carbon monoxide. It may be enriched by the addition of oils. It is an important source of hydrogen, and it also finds use in making *methanol*. *Acetylene* is made by adding water to calcium carbide. It is used for illuminating purposes, and for the welding and cutting of metals.

*A flame is a burning gas.* A luminous flame gives light because there are present in it particles of carbon that are heated to incandescence. The Bunsen burner has two cones: the *outer cone is the oxidizing flame*; the *inner cone is the reducing flame*. The burner of a gas range is merely a modified Bunsen burner.

A gas mantle may be used to utilize the heat of the burning gas, and increase the efficiency of the flame for purposes of illumination.

To prevent a smoke nuisance, two things are needed: (1) To supply the fuel to the grate at a constant rate; (2) to supply enough additional air to insure complete combustion. A *forced draft* is used to make a hotter flame.

## QUESTIONS

## GROUP A

1. Discuss the value of wood as a fuel.
2. What advantages has hard coal over soft coal as a fuel? Has it any disadvantages?
3. From the table showing the composition of fuels, explain why wood has a lower heat content than soft coal.
4. Under what conditions does gasoline vapor explode?
5. What is meant by the explosive range of a gas?
6. What does a motorist mean by "rich" and "lean" mixtures?
7. What is meant by "flooding" the carburetor and cylinders of an automobile?
8. Why is it dangerous to work in a closed garage with the engine of the car running?
9. Suppose the burner of a gas stove "strikes back." How would you adjust the burner? How would you fix the burner of your gas stove if the flames have yellow tips?



10. Is bread a fuel? What is the meaning of the expression, "A thick slice of bread furnishes 100 Calories"?
11. Is it necessary to enrich water gas if it is to be used for fuel only?
12. Why is water gas somewhat more dangerous to inhale than coal gas?
13. Why does acetylene burn with such an extremely hot flame?
14. Explain how you would bank a fire for the night.
15. When hard coal is added to a coal fire, a blue flame is produced. Explain.

## GROUP B

16. Suppose you are a salesman for some type of burner for fuel oils. What arguments would you use in favor of its installation to replace hard coal?
17. How would you proceed to determine the number of calories that a teaspoonful of sugar will furnish?
18. Powdered coal is sometimes made into briquettes by mixing it with some tarry binder, and pressing it into lumps. What advantages has such a fuel?
19. How would you proceed to determine the per cent of ash in a fuel?
20. If a kerosene lamp or a kerosene heater smokes, what is the probable cause?
21. In what ways is the human body like a furnace?
22. Vessels at sea have used smoke screens to escape from hostile craft. How can such a smoke screen be produced?
23. Can kerosene be substituted for gasoline for use in gas engines? Give a reason for your answer.
24. From the formula and percentage composition of acetylene, explain why you would expect it to burn with a smoky flame.
25. What conditions are necessary to eliminate smoke in an industrial city?
26. What is pyrofax gas? For what purposes is it used?
27. Give a good reason why the gas mantle is less used than formerly.
28. Can you tell why oxygen in a fuel is both an advantage and a disadvantage?



## SUPPLEMENTARY PROJECTS

Prepare a report on one of the following topics:

1. Coal in Industry.

Reference: HOWE, H. E., *Chemistry in Industry*. Chemical Foundation, Inc. Vol. I, Chap. 4.

2. Coal tar products.

References: CALDWELL, O. W., and SLOSSON, E. E., *Science Remaking the World*. Doubleday, Page and Co. Page 48.

HOWE, H. E., *Chemistry in Industry*. Chemical Foundation, Inc. Vol. II, Chap. 4.

3. Gasoline as a World Power.

Reference: CALDWELL, O. W., and SLOSSON, E. E., *Science Remaking the World*. Doubleday, Page and Co. Page 12.

## CHAPTER 21

### THEORY OF SOLUTION — IONIZATION

#### Vocabulary

**Electrolyte.** A compound which in water solution conducts the electric current.

**Ionization.** The dissociation of a compound into ions.

**Ion.** An atom or a group of atoms that carries a charge of electricity.

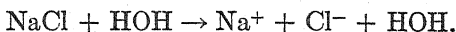
**Dissociate.** To break up into ions.

**278. Some Facts That Need Explanation.** In geometry there are many theorems to be proved. In chemistry, certain facts are explained by theories. In many of the experiments that we have performed, the chemicals have been used in water solution. In fact, water seems to act like a general catalyst. Baking powder is a mixture of a carbonate, and an acid or acid salt. When water is added, chemical action begins. In our study of acids, we learned that the general characteristics of an acid refer to a water solution of the acid. In the General Electric Laboratories, an experiment was performed that seemed to indicate that a mixture of hydrogen and oxygen will not explode unless a *trace* of water is present. For decades chemists were puzzled to account for the behavior of substances in water solution. Let us mention other facts that need to be explained, too.

1. We know that electricity passes through a copper wire readily. We say the wire is a conductor. Pure water does not conduct the current. It was necessary to add a little acid or base when we decomposed water by electricity. Let us set up an apparatus like that shown in Fig. 183. An electric bulb is connected in series with a bottle into which two carbon

1. That electrolytes in solution are dissociated into ions.
2. An ion is an atom or a group of atoms that carries an electric charge.
3. The water solution contains an equal number of positive and negative charges.

To illustrate, let us try to picture a water solution of sodium chloride. (See Fig. 185.) Part of the sodium chloride molecules *dissociate* into ions. The following *ionic equation* shows the manner of such dissociation:



The sodium atom loses an electron, ( $\text{Na} - e = \text{Na}^+$ ), and becomes positively charged. The chlorine atom gains an electron, ( $\text{Cl} + e = \text{Cl}^-$ ), and thus acquires a negative charge.

Some of the sodium chloride molecules are not dissociated; the per cent that dissociates increases as the solution is made more dilute. If we concentrate the solution by evaporating the water, we decrease the number of ions present. The ionic equation shown above is reversible.

As the water, which serves as the ionizing agent, is removed, the ions *associate* to form molecules of sodium chloride. We write the formula for water here as HOH; water itself is slightly ionized to form positive hydrogen ions and negative hydroxyl ions. Such slight ionization may be neglected when we deal with substances like sodium chloride that ionize so readily. The slight ionization of water must be considered, however, when we are dealing with solutions of electrolytes that dissociate to only a slight degree.

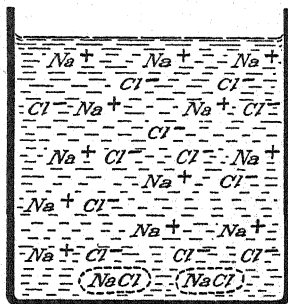
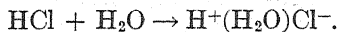


FIG. 185.—Part of the molecules of sodium chloride dissociate into ions.

In the electron theory of valence, it was assumed that one hydrogen atom can *lose* an electron and thus acquire a positive valence of *one*. And that a chlorine atom can *gain* an electron and acquire a negative valence of *one*. Electrical attraction is believed to be the cause of chemical affinity; in the union of  $H^+$  and  $Cl^-$  to form a molecule of  $HCl$ , the bond seems to be the attraction between unlike charges. When  $HCl$  is dissolved, the water in some unknown way seems to loosen (dissociate) the attractive force between the atoms. We may picture the water as an ionizing agent bringing about such an estrangement in some such manner as the following:



**280. Ions and Atoms Have Different Properties.** When Arrhenius proposed his theory, Dr. Cleave, the man under whom he was working, said: "Your theory is absurd. Any beginner in chemistry knows that free sodium attacks water, and that free chlorine colors a water solution yellow." But Arrhenius answered his objection by asking: "Is it not possible that an atom which carries a charge of electricity will have different properties from an uncharged atom?" Let us consider the fact that oxygen which absorbs energy and forms ozone has a new set of properties. We know, too, from our study of valence that the gain or loss of one or more electrons makes a tremendous difference in the properties of an atom. Hence it is to be expected that a sodium atom which has lost an electron will have a new set of properties. If we add an electron to a sodium ion ( $Na^+ + e \rightarrow Na$ ), then the atom of sodium that is formed will have all the properties of the sodium atom; it will attack water and form sodium hydroxide. In like manner, we would expect that a chlorine atom which carries a negative charge will exhibit different properties from one that has no charge. Chlorine is poisonous and turns a water solution yellow. But if we add an elec-

tron to an atom of chlorine, the ion ( $\text{Cl}^-$ ) that is formed will not have such properties.

Dr. Cleave also offered the following absurd objection: "If a water solution contains electrically charged particles, one will get a shock when he puts his hand into a salt water solution." But Arrhenius answered this objection by an explanation that should be familiar to every high-school pupil of physics. "There are the same number of positively charged particles as negatively charged particles. Electricity manifests itself only when there is an *excess* of one kind of electrical charge."

### 281. How the Ionization Theory Explains Electrolysis.

Let us dissolve some copper sulfate,  $\text{CuSO}_4$ , in water. We may represent such a solution by a diagram like that shown in Fig. 186, if we accept the theory of ionization. Since the copper atom is bivalent, it can lose two electrons; therefore each copper ion,  $\text{Cu}^{++}$ , carries two plus charges; each sulfate radical ( $\text{SO}_4^{--}$ ) carries two minus charges.

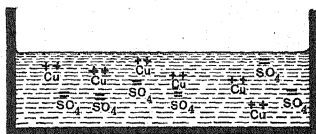


FIG. 186. — Dissociation of copper sulfate into its ions.

Next let us suspend in the solution two platinum strips, or carbon rods, and connect them to a battery as shown in Fig. 187. The rod which is connected to the positive terminal of the battery is called the *positive electrode*, or the *anode*. It has a deficiency of electrons, or a positive charge. The rod connected to the negative

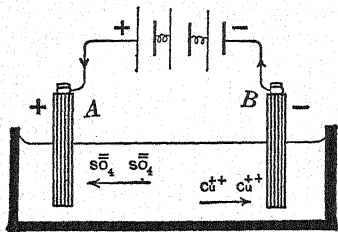
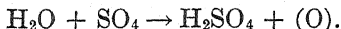


FIG. 187. — Electrolysis of copper sulfate.

terminal of the battery is called the *negative electrode*, or the *cathode*. Since like charges repel, and unlike charges attract,

the copper ions will go to the cathode. There they receive enough electrons to neutralize their charge, and metallic copper is formed and deposited on the cathode rod. ( $\text{Cu}^{++} + 2e \rightarrow \text{Cu}$ .) The other ion, which is called sulfion ( $\text{SO}_4^-$ ) is attracted to the anode, where it loses its extra electrons to the anode. ( $\text{SO}_4^- - 2e \rightarrow \text{SO}_4$ .) But the ( $\text{SO}_4$ ) radical cannot exist alone, and it probably attacks the water and forms sulfuric acid.



Two oxygen atoms unite to form a molecule of oxygen gas, which bubbles off at the anode.

The student should remember that, during electrolysis, the *dissociation of the electrolyte occurs before the electrodes are introduced*. The charged electrodes separate the ions, the positive ion going to the cathode, and the negative ion to the anode. This explains why the *hydrogen and the metal ions go to the cathode, while the oxygen and other non-metal ions go to the anode*. The name "ion" means wanderer; the ions really migrate through the solution and thus make it a conductor of electricity. Hence *electrolytes are conductors because they dissociate into ions which migrate through the solution by attraction or repulsion*. Non-electrolytes do not ionize; therefore their solutions are non-conductors. *Electrolysis, then, is the separation of a dissociated compound into its constituents by means of the electric current*.

Electrolysis plays an important part in chemistry. By this process, storage batteries are charged, certain elements are isolated, other elements are purified, and metals are plated with less active or more beautiful metals. Sometimes when a compound is decomposed by the aid of the electric current, several secondary chemical reactions may take place.

**282. Why Electrolytes Have an Abnormal Effect on Freezing Points and Boiling Points.** Julius van't Hoff applied Avogadro's Law to dilute solutions. This means that

a molar solution of alcohol will have the same number of molecules of solute that an equal volume of a molar solution of sugar has. In fact *equal volumes of all molar solutions have the same number of molecules of solute*. It seems reasonable, then, to expect that the lowering of the freezing point, or the elevation of the boiling point, by a solute is proportional to the number of *particles* in a given volume of solvent. But a molar solution of sodium chloride, for example, lowers the freezing point nearly twice as much as a molar solution of sugar. Is that not what we would expect? The sodium chloride molecules ionize; but the sugar molecules do not. If all the molecules present in a molar solution of sodium chloride were *dissociated*, or ionized, then there would be just twice as many particles present as in a non-ionized solution of the same molar concentration. Then the abnormal lowering of the freezing point that is caused by an electrolyte must be due to the fact that by dissociation the number of particles present in the solution is increased. A solution of sodium chloride does not lower the freezing point quite twice as much as a similar solution of sugar does, because fewer than 100% of the molecules are ionized.

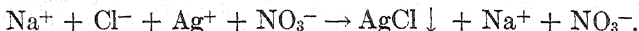
When a molecule of calcium chloride,  $\text{CaCl}_2$ , ionizes it forms three ions. ( $\text{CaCl}_2 \rightarrow \text{Ca}^{++} + 2\text{Cl}^-$ .) There is one calcium ion that carries two plus charges; there are two negative ions, each with a single electron. It seems reasonable to expect, from the ionization theory, that a molar solution of calcium chloride will lower the freezing point almost *three times as much* as the molar solution of a non-electrolyte. Careful experiments show that very dilute solutions of calcium chloride, in which the ionization approaches 100%, do lower the freezing point nearly three times as much as do non-electrolytes. Hence the theory accords with the facts, and it explains why acids, bases, and salts (all of them are electrolytes) lower the freezing point abnormally, and why Raoult's laws cannot be used to determine their molecular



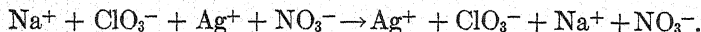
weights. For the same reason they raise the boiling point abnormally.

**283. Why Electrolytes Are Active Chemically.** It seems natural to expect that ions would be more active than molecules. If the molecules are *dissociated* by the solvent, the ions are more or less free to unite with other ions, or to rearrange themselves to form other molecules. The *undissociated* molecules do not take part in chemical reactions.

When we make tests in the laboratory, *we test for ions* and not for atoms or molecules. To test for *chloride ions* in a solution, we add silver nitrate solution. Let us write the ionic equation.



The positive silver ion unites with the chloride ion to form a molecule of *undissociated* silver chloride. This salt does not dissociate in water, because it is insoluble. Any chloride ion will unite with a silver ion to form a white precipitate of insoluble silver chloride. Hence a solution of silver nitrate, or of any soluble silver salt, may be used in this manner to test for chloride ions. Chlorine molecules dissolved in water do not have the same effect upon a solution of silver nitrate. That this solution is not a test for *chlorine* may be shown by adding some silver nitrate to a solution of sodium chlorate,  $\text{NaClO}_3$ . The *ionic equation* follows:



There is no doubt from the formula for sodium chlorate that chlorine is present in its molecule, but no white precipitate is formed when silver nitrate solution is added. If any reaction occurs at all, the substances all ionize and remain in solution. A solution of silver nitrate forms a precipitate with any *chloride* ion, but it does not form a precipitate with a *chlorate* ion. Silver nitrate is a test for  $\text{Cl}^-$ ; it is not a test for  $\text{Cl}$ ,  $\text{Cl}_2$ , or  $\text{ClO}_3^-$ .

Anhydrous copper sulfate is white; the hydrated salt or a solution of the salt is blue in color. Since soluble copper salts give a blue solution we may infer that the blue color is due to the copper ion. In a similar way it may be shown that the ferrous ion is green, while the ferric ion is reddish-brown. Cobalt salts are pink in water solution when ionized, but a large number of them become blue when they are dehydrated.

The theory of ionization explains the fact that such mixtures as baking powder, effervescing powders, etc., do not act in the dry state, but that a chemical change begins as soon as water is introduced, thereby causing dissociation.

**284. How Acids Ionize.** In our study of acids, we learned that all acids contain hydrogen. We also learned that the acid properties are characteristic of water solutions of the acids. If we dissolve hydrogen chloride in water, we have an acid solution called hydrochloric acid. The compound ionizes as follows:  $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$ . Nitric acid in water solution yields the following ions:  $\text{HNO}_3 \rightarrow \text{H}^+ + \text{NO}_3^-$ . *All acids give positive hydrogen ions in water solution.* In fact, we may define an acid as a compound that forms positive hydrogen ions in water solution.

Sulfuric acid ionizes in two stages or steps, depending upon the amount of dilution. The equations follow:



The first step represents the ionization in a rather concentrated solution; the second step shows how sulfuric acid ionizes in a more dilute solution. These steps show that it is possible for an acid like sulfuric acid to form two classes of salts: (1) The *acid salts*, in which the  $\text{HSO}_4^-$  radical is present; sodium acid sulfate,  $\text{NaHSO}_4$ , is an example. (2) *Normal salts*, in which the  $\text{SO}_4^{=}$  radical is present; sodium sulfate,  $\text{Na}_2\text{SO}_4$ , is an example.

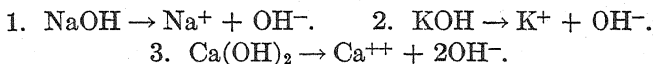
285. What Is Meant by a Strong Acid? The student should have a concept of the terms *dilute* and *concentrated* acids. But the terms *strong* and *weak* acids have a different significance. From the definition of an acid as given in the preceding section, it would appear that the strength of an acid depends upon the *number of hydrogen ions present* in a given volume of solution. *An acid that furnishes a large concentration of hydrogen ion is called a strong acid.* Hydrochloric acid and nitric acid ionize so easily that they furnish a large hydrogen ion concentration. They are among the strongest acids known. Such acids as acetic and carbonic do not ionize readily. They are *weak acids*. A concentrated solution of acetic acid may have fewer hydrogen ions per c.c. than a dilute solution of hydrochloric acid or nitric acid. To illustrate, concentrated nitric acid (68%) has fewer than 10% of its molecules ionized. In a 6% solution of the same acid more than 80% of its molecules are ionized. Less than half of 1% of the molecules are ionized in a 6% solution of acetic acid.

Quite often students get the erroneous idea that the more we dilute an acid, the stronger it becomes. Such is not the case, for 100 c.c. of a 50% acid in which 10% of the molecules are ionized will have more hydrogen ions than the same volume of 2% acid in which 95% of the molecules are ionized. Making a solution more dilute increases the *degree of ionization*, but it does not necessarily increase the number of hydrogen ions per cubic centimeter. 1% of \$1,000,000 is a more valuable legacy than 50% of \$100. Increasing the temperature of a solution also increases the degree of ionization.

Because sulfuric acid will decompose the salts of other acids, beginners sometimes get the idea that sulfuric acid is stronger than those acids. Such decomposition is due to the fact that sulfuric acid has a high boiling point, and not to the fact that it is a stronger acid. In reality, sulfuric

acid is only about half as strong as either nitric acid or hydrochloric acid.

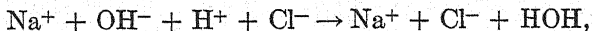
**286. How Bases Ionize.** We know that all bases have one or more hydroxyl (OH) radicals in each molecule. When bases ionize, the metal becomes positively charged, and the hydroxyl radical forms the negative ion. For example:



Since calcium hydroxide furnishes two hydroxyl radicals per molecule, we write  $2\text{OH}^-$ , instead of  $(\text{OH})_2^-$ . *A base is a compound that forms negative hydroxyl ions in water solution.*

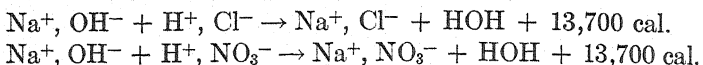
**287. What Is Meant by a Strong Base?** Sodium hydroxide and potassium hydroxide are the strongest bases known. They ionize readily, and give a large concentration of hydroxyl ions. *The strength of a base depends upon the concentration of the hydroxyl ion.* Ammonium hydroxide yields only about 4% as many hydroxyl ions as sodium hydroxide of the same concentration. It is a moderately weak base.

**288. What Is Neutralization?** Let us mix equal volumes of *normal* solutions of sodium hydroxide and hydrochloric acid. The ionic equation,

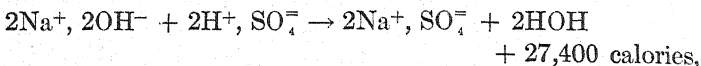


shows that the hydrogen ion of the acid unites with the hydroxyl ion of the base to form *non-ionized*, or *little ionized*, water. Briefly, *we may define neutralization as the union of the positive ion of an acid with the negative ion of a base to form water.* The salt that is formed at the same time ionizes in the water, since salts usually ionize to a high degree. *A salt may be defined as a compound formed by the union of the positive ion of a base with the negative ion of an acid.*

It is interesting to note that the amount of heat liberated by neutralizing *one mole* of hydrochloric acid is the same as that set free when one mole of nitric acid or one mole of hydrobromic acid is neutralized.



This is also the heat of formation of one mole, 18 gm., of water by neutralization. The neutralization of sulfuric acid,



forms *two moles* of water and *twice* as much heat is liberated.

**289. The Degree of Ionization.** Since the ions carry the electric current and make the electrolyte a conductor, it follows that a careful measurement of the conductivity of a solution furnishes us with a method of determining to what degree a substance is ionized. In comparing the conductivity of two solutions, we must be sure that the solutions have the same molar concentration. By such methods, it has been determined that hydrochloric acid is a strong acid, and acetic acid a weak acid. It is also possible to determine the degree of ionization by measuring the amount of lowering of the freezing point.

**290. What Factors Affect the Degree of Ionization?** If we determine the degree of ionization of a concentrated solution, and then determine the degree of ionization of a dilute solution of the same solute, we learn that *increasing the volume of the solvent increases the degree of ionization*. Theoretically the ionization reaches 100% when the solution becomes infinitely dilute. As we concentrate a solution, more of its ions reunite to form undissociated molecules.

*An increase in temperature also increases the degree of ionization.* This fact is also determined by actual experiment.

**291. Ionizing Agents.** In our discussion of ionization, we have referred in all cases to water as the ionizing agent. It is by far the best ionizing agent known. Ionization does not occur readily in most other solvents. For example, hydrogen chloride dissolved in water forms a strong acid. The gas does not have acid properties, nor does liquid hydrogen chloride (100%). It does not have acid properties if it is dissolved in toluol, since toluol is not an ionizing agent. Such solvents as benzol, toluol, ether, and alcohol are extremely poor ionizing agents.

Heat produces ionization. Gases that are heated to a high temperature become fair conductors of electricity, because they are ionized to some extent during the heating. Heating a solution increases the degree of ionization of the solute.

Fused or melted salts are ionized. Dry solid sodium chloride is a non-conductor, but the melted salt is a good conductor. Considerable use is made of the fact that fused salts ionize, especially in the electrolysis of compounds whose elements unite readily with water. Compounds that are insoluble in water may be melted and then decomposed by electrolysis.

Molecules are also ionized by being bombarded by the particles projected from radio-active substances as they disintegrate. See Chapter 40.

**292. Ions Have Valence.** When hydrogen and the metallic elements ionize, they lose electrons. The number of electrons a metal can lose depends upon its valence. For example, a sodium atom loses one electron as it ionizes, and acquires a positive valence of 1. A chlorine atom *gains* one electron; then the chloride ion has a negative valence of 1. The number of electrons a negative ion has acquired determines its valence; the number of electrons a positive ion has lost determines its valence.

★ **293. Polar and Non-polar Compounds.** Such a com-

pound as sodium chloride is called a *polar compound*. During the formation of such a compound, it is believed that the chlorine atoms really take possession of the electrons lost by the sodium atoms. Water as an ionizing agent loosens the bond between such atoms, so they ionize and become conductors in solution.

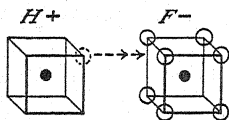


FIG. 188. — Hydrogen loses an electron and fluorine gains one.

The chloride ion migrates to the positive pole or electrode, and the sodium ion to the negative pole, or electrode. The *polar compounds ionize in solution or when heated*. Figure 188 shows a possible configuration of hydrogen fluoride, HF, a polar compound.

Then there are some compounds that do not ionize. Dr. G. N. Lewis, of the University of California, has explained this fact by assuming that the atoms in such a molecule *share electrons*. The hydrogen molecule is  $H_2$ ; it seems probable that the two atoms share the electrons in a kind of partnership. In such a compound as carbon dioxide, it is probable that the carbon atom shares two electrons with each of two oxygen atoms. (See Fig. 189.) The sharing of electrons in a partnership of this kind is called *co-valence*. When atoms share electrons, they do not ionize.

Just as it is possible for two persons in a partnership to have unequal shares, so it seems possible for one element in a non-polar compound to be slightly more partial for electrons than the other. The carbon atom in carbon dioxide may not have quite so large a share in the electrons as the more grasping atoms of oxygen. Even in polar compounds, the negative element may not have an uncontested deed for the electrons in its possession. For these reasons, the *tendency of com-*

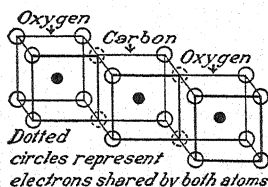
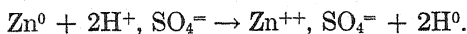


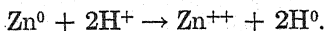
FIG. 189. — The electrons are believed to be shared by the atoms.

pounds to ionize is relative, dependent upon how completely one element robs another of its electrons. Equal partnership means no ionization; the more unequal the sharing, the easier the ionization.

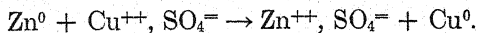
★ 294. **Displacement of One Element by Another.** Let us turn back to the displacement table, as given on page 76. The elements increase in activity as we go toward the top of the list. The elements at the top of the list tend to ionize easily; those at the bottom have a smaller tendency to ionize. When zinc and sulfuric acid interact, for example, the zinc goes into solution and displaces the hydrogen, because zinc ionizes more readily than hydrogen does. Let us write the ionic equation.



In the beginning the zinc, Zn, had zero valence, and each hydrogen atom had lost an electron to the sulfion  $\text{SO}_4$ . At the end of the reaction, the zinc has ionized by losing two electrons, and hydrogen atoms of zero valence have been liberated (non-ionized). It is the same as if we had written the equation as follows:



In exactly the same manner, metallic zinc will displace copper from a solution of copper sulfate. See equation:



To liberate an element near the top of the table by electrolysis requires a higher voltage than it does to liberate an element near the bottom, silver for example. The back pressure, or the tendency to ionize, is greater in the case of potassium or sodium than it is in the case of silver or gold.

★ 295. **The Structure of Crystals.** By the use of X-rays,



it has been possible to show that the crystals of salts are really made up of a kind of lattice-like structure, built up of

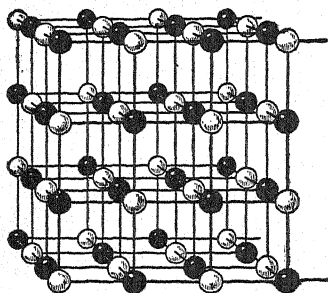


FIG. 190. — Structure of the molecule of common table salt.

ions held together by electrical attraction. Figure 190 shows the arrangement in a crystal of sodium chloride. From this fact, it appears that crystals are not made up of molecules, but that a crystal is really a large molecule made up of ions. When such a crystal is melted, it loses its crystalline structure and the ions which are loosened

from their electrical attraction become free to migrate. Thus the fused salt ionizes and becomes a conductor.

### SUMMARY

An *electrolyte* is a compound whose water solution is a good conductor of electricity. Such substances as alcohol, ether, sugar, and glycerine are *non-electrolytes*. Their solutions are non-conductors. The solutions of *acids, bases, and salts* are conductors. These substances are *electrolytes*.

The *ionization theory* attempts to explain: (1) How electrolytes conduct the electric current; (2) Why electrolytes lower the freezing point of a solvent to an unusual degree; (3) Why electrolytes are active chemically.

The ionization theory assumes: (1) *That electrolytes in solution are dissociated into ions*; (2) *That an ion is an atom or a group of atoms that carries an electrical charge*; (3) *That the number of positive ions equals the number of negative ions*.

The properties of an ion are different than the properties of an atom. Chemical tests are tests for ions. *Electrolysis* is the separation of the constituents of a compound by means of the electric current.

*An acid is a compound whose water solution contains hydrogen*

*ions.* The *strength* of an acid depends upon the concentration of the hydrogen ion.

A *base* is a compound whose water solution contains *hydroxyl ions*. The *strength* of a base depends upon the concentration of the hydroxyl ion.

*Neutralization* is the union of the hydrogen ion of an acid with the hydroxyl ion of a base to form water. A *salt* is formed by the union of the positive ion of a base with the negative ion of an acid.

The *degree of ionization* is determined by measuring the conductivity. *Increasing the volume of the solvent*, or *heating the solution*, *increases the degree of ionization*.

Water is the best ionizing agent. An electrolyte can be ionized by melting it, or by bombarding it with particles from cathode rays, or from atomic disintegration.

Compounds that ionize are known as *polar compounds*. *Non-polar compounds* do not ionize. The valence of an ion depends upon the number of electrons which it has lent or borrowed. The ability of one element to displace another depends upon its tendency to go into solution, or to ionize.

## QUESTIONS

### GROUP A

1. Why do we call a solution of hydrogen sulfide a weak acid, and the solution of hydrogen chloride a strong acid?
2. What is an electrolyte? How can you determine whether glycerine is an electrolyte?
3. Define acid, base, and salt in terms of the ionization theory.
4. What is the difference between the hydrogen ion and the hydrogen atom? How does the hydrogen atom differ from the hydrogen molecule?
5. Which do you think would be the better conductor, sea water or distilled water? How do their freezing points compare?
6. Is dry hydrogen chloride gas an acid? Is liquid hydrogen chloride an acid? How would you treat hydrogen chloride to give it acid properties?
7. What is the difference between a ferrous ion and a ferric ion?

## GROUP B

8. How do you explain the fact that dilute sulfuric acid attacks zinc, but cold, concentrated sulfuric acid does not attack it?

9. Use a diagram to show what happens when an electric current is passed through a solution of sodium chloride. From the standpoint of the ionic theory, explain the action.

10. Paper flowers, or doll dresses made of paper, are sometimes coated with a solution of cobalt chloride. From the standpoint of ionization, explain why they change color as the moisture content of the air changes.

11. If sodium chloride ionizes in solution, how does it happen that the sodium does not attack the water?

12. What would you expect to happen if strips of zinc were immersed in solutions of each of the following metals: copper; tin; magnesium; gold; aluminum?

13. Make a diagram of an apparatus to be used for silver plating. Where should you put the object to be plated? What electrolyte can be used? Of what should the anode be made? Why?

## EQUATIONS AND PROBLEMS

1. Write the equation to show how each of the following compounds ionizes: barium hydroxide; potassium sulfate; ferric chloride; ammonium sulfate; bromic acid.

2. Write ionic equations to show the neutralization of: calcium hydroxide with nitric acid; calcium hydroxide with sulfuric acid.

3. How many pounds of sulfuric acid would be needed to neutralize 400 lb. of calcium hydroxide?

4. How many pounds of calcium sulfate are formed in Problem 3?

## CHAPTER 22 ★

# EQUILIBRIUM — END REACTIONS — HYDROLYSIS

### Vocabulary

**Equilibrium.** Used in chemistry to refer to a reaction in which the products unite to form the original factors at the same speed at which the factors are forming the products.

**Dynamic.** Referring to motion as opposed to a condition of rest.

**Static.** Referring to a condition which does not change; a condition of rest.

**Hydrolysis.** The interaction of water with a salt to form the base and acid of which the salt is the product.

### A. EQUILIBRIUM

**296. Physical Equilibrium.** Contrary to the opinions of some persons, motion rather than rest seems to be normal in the universe. Molecules are *dynamic* or *kinetic*; they are not *static*, or at rest. If we place a bell-glass over a pan of water, the air above the pan will soon become saturated with water vapor. If we could magnify the molecules of water enough to see them, we would have a picture something like that represented in Fig. 191. Some molecules moving toward the surface would enter the air; some would collide with air molecules or other water molecules, rebound, and return to the liquid. Let us suppose that 1,000,000 molecules leave the water per second, and that 1,000,000 molecules return to it per second. Then the air is *saturated with water vapor*. Such saturation is a condition

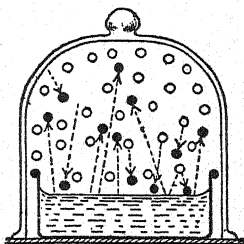
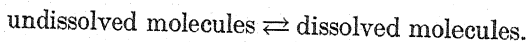


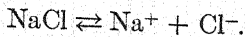
FIG. 191. — Saturated vapor.

of equilibrium between the molecules leaving the water and those returning. Hence, equilibrium appears to be a condition of rest, but it is actually one of constant motion.

In preparing a saturated solution of sugar, we shake an excess of the solute with the solvent. At first molecules of the solute go into solution rapidly. But some of the molecules entering the solution will collide with water molecules, or with other sugar molecules, and rebound to the undissolved mass. As the solution becomes more concentrated, such collisions naturally become more frequent. When the number of molecules returning to the undissolved mass per second exactly equals the number of molecules going into solution per second, the solution is said to be *saturated*. This example of *physical equilibrium* may be represented as follows:

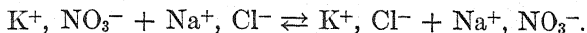


**297. Ionic Equilibrium.** No doubt some pupils have wondered why the ions in a solution do not combine to form undissociated molecules, since they are charged with electricity of unlike sign, and we know that unlike charges attract. As a matter of fact, they do. Ionization is kinetic, too, instead of static. In the ionization of sodium chloride, for example, some molecules are ionizing, and at the same time some ions are recombining to form undissociated molecules. When we dilute a solution, we increase the volume of the solvent, and the opportunity for the contact between ions is decreased. Hence dilution increases ionization. When we concentrate a solution, more ions will unite to form undissociated molecules. The equation shown is typical of *ionic equilibrium*.



**298. Chemical Equilibrium.** We learned that water may be decomposed by the use of the electric current. But we

can reverse the reaction, and cause the hydrogen and oxygen to combine and form water, provided we heat a mixture of the gases. Lavoisier formed mercuric oxide by heating mercury and oxygen; then he decomposed the mercuric oxide into mercury and oxygen by heating it to a higher temperature. Many chemical reactions are reversible, or they run to equilibrium. If we mix solutions of potassium nitrate,  $\text{KNO}_3$ , and sodium chloride,  $\text{NaCl}$ , we have an equilibrium reaction that may be represented by the ionic equation,



It is evident that we have four examples of ionic equilibrium between the dissociated and the undissociated molecules of potassium nitrate, sodium chloride, potassium chloride, and sodium nitrate. Such a solution undoubtedly contains the following: ions of potassium, sodium, chlorine, and the nitrate radical; undissociated molecules of potassium nitrate, potassium chloride, sodium nitrate, and sodium chloride. Some potassium ions will doubtless unite with chloride ions to form potassium chloride. Meanwhile some of the sodium ions will be uniting with nitrate ions to form sodium nitrate. But in time this action toward the right side of the equation will be offset by the tendency of the ions on the right side of the equation to recombine and form the original substances. Such a condition produces *chemical equilibrium*.

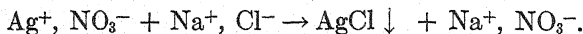
## B. END REACTIONS

**299. Reactions That Run to Completion.** Reactions that run to completion, or in one direction only, are a joy to the heart of the manufacturing chemist. While there are no cases of such *absolutely ideal* conditions, yet there are a number of chemical reactions that show *little* tendency to reverse even under normal conditions. Some reactions that

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under ordinary conditions are reversible may be *coaxed or driven* to practical completion. Furthermore, chemists can *predict* that certain types of reaction will go to an end. If we bring together the ions needed for a double decomposition reaction, *the reaction will always occur, and proceed to completion*, provided:

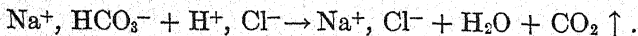
1. *One of the products formed is insoluble.* In testing for a chloride, we added a solution of silver nitrate to the unknown. Suppose, for example, that the unknown solution contained sodium chloride. The reaction may be represented as follows:



The silver ions unite with the chloride ions to form undissociated, insoluble silver chloride. The silver chloride is precipitated as fast as it is formed, and it is thus removed from the "field of action." There is no possibility of a reversal of the reaction, because the ions that could cause such reversal have been removed. The reaction goes *in one direction to an end* as long as either silver ions or chloride ions are present. *A double decomposition reaction will always occur, if one of the compounds that would be formed is insoluble; such a reaction runs to completion.*

NOTE. The extremely slight solubility of silver chloride is the only thing that keeps the reaction from being 100% complete.

2. *One of the products formed is volatile.* When we add hydrochloric acid to a solution of baking soda,  $\text{NaHCO}_3$ , the reaction runs to completion as represented by the equation,



In this case the carbon dioxide bubbles off as a gas, and is removed from the "field of action" as fast as it is produced.

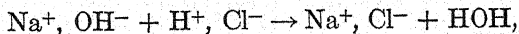
If one of the products formed is a gas, or is vaporized, the reaction runs to completion. Hence, we conclude that *double decomposition reactions will occur if one of the products that would be formed is volatile; such a reaction runs to completion.* Count Berthollet was the first to show the truths concerning completion reactions. The two facts just stated concerning end reactions are known as BERTHOLLET'S LAWS.

NOTE. The backward pressure of air tends to prevent the complete removal of the carbon dioxide. This factor prevents full completion of such reactions.

### 3. *One product does not dissociate.*

When we neutralize a strong base, such as sodium hydroxide, with a strong acid like hydrochloric, the reaction runs to completion because water

does not ionize to any appreciable extent *compared* to the ionization of the other compounds. The equation,



is typical. In 10% solutions, both sodium hydroxide and hydrochloric acid ionize to the extent of 50% or more. The dissociation of water is less than 2 parts per 1,000,000,000.



William Thompson

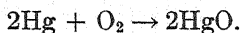
FIG. 192. — Claude Louis Berthollet (1748–1822) was a French chemist. He assisted in the reform of chemical nomenclature. He is best known for the laws pertaining to end-reactions. In conference with Lavoisier.



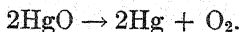
Hence the hydrogen ion of the acid and the hydroxide ion of the base are both removed by their uniting to form non-ionized water. Neutralization reactions run to completion. (See hydrolysis, page 370.) We may summarize the three cases we have had in one statement: *Double decomposition reactions will occur when the needed ions are brought together, provided one of the products formed does not ionize. Such reactions run to completion.*

**300. How Reactions May Be Forced Toward Completion.** Suppose we have twenty men engaged in a tug-of-war game. If there are ten men, all equally strong, on each side, there will be a dead-lock, or equilibrium. We can destroy such equilibrium by taking away a man from one side, by adding a man to one side, or in some way by weakening one group or by stimulating another group. In a similar manner, the chemist changes the physical or chemical conditions in order to *force or drive* an equilibrium reaction in the direction he desires it to go. By the use of examples, let us illustrate several methods.

1. *Effect of temperature.* At a moderate temperature Lavoisier formed mercuric oxide by heating mercury in the presence of oxygen.



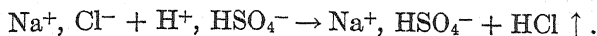
In order to reverse such a chemical reaction, and secure oxygen and mercury, the temperature must be raised still more. At a higher temperature, the mercuric oxide decomposes as follows:



There are many reactions in chemistry where temperature control is most important.

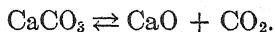
2. *Effect of pressure.* In order to prepare hydrogen chloride, we heat a mixture of concentrated sulfuric acid with sodium chloride. The reaction in this case runs natu-

rally in the direction we want it to go, because hydrogen chloride is volatile.



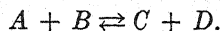
If, however, hydrogen chloride is forced under pressure into a solution of sodium acid sulfate, the reaction may be *driven* toward the left.

In making quicklime,  $\text{CaO}$ , calcium carbonate is heated. The equation is as follows:

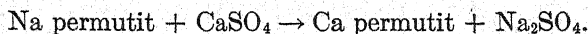


The backward pressure of the air keeps part of the carbon dioxide from escaping and tends to drive the reaction toward the left. By blowing air through a lime-kiln periodically to sweep away the carbon dioxide, the manufacturer increases the yield of quicklime.

3. *Effect of concentration.* Let us consider a general equilibrium reaction in which the factors  $A$  and  $B$  are uniting to form the products  $C$  and  $D$  at exactly the same speed that  $C$  and  $D$  are reacting to form  $A$  and  $B$ .



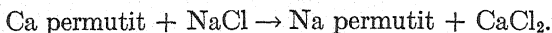
It is evident that *doubling* the molecular concentration of  $A$  will increase the number of contacts with  $B$  and increase the speed of the reaction toward the right. By the use of an *excess* of one reagent, the speed of the reaction may be increased, and the equilibrium may be displaced. It is possible, too, to decrease the concentration of one factor. In our study of the softening of hard water, we found that permutit would exchange its sodium for the calcium in the hard water.



But if we increase the concentration of the sodium ion by adding a 10% solution of sodium chloride, the reaction can

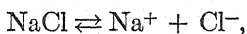
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be reversed and the permutit may be *regenerated* for use in softening more water.



By the use of an excess of a reagent the speed may be increased and a reaction driven in the desired direction. This LAW OF MASS ACTION is sometimes stated: *The speed of a reaction is proportional to the product of the molecular concentrations of the reacting substances.*

**301. What Is Meant by the Common Ion Effect?** Through a saturated solution of sodium chloride, let us bubble some hydrogen chloride. As the hydrogen chloride dissolves, sodium chloride is precipitated. In the equation,



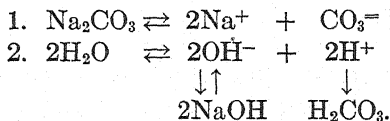
we have represented the ionic equilibrium between dissociated and undissociated molecules of sodium chloride before the hydrogen chloride was added. But when we add the hydrogen chloride, we increase the concentration of the chloride ion and drive the reaction to the left. Because the solution was already saturated with sodium chloride, driving the reaction to the left causes sodium chloride to be precipitated. This particular case of mass action is known as the *common ion effect*. The chloride ion is common to both sodium chloride and to hydrogen chloride. The addition of sodium nitrate to a saturated solution of sodium chloride will cause precipitation, because both have in common the sodium ion.

### C. HYDROLYSIS

**302. Hydrolysis.** In Section 299 we neglected the slight ionization of water, and assumed that neutralization reactions run to completion. When we neutralize a *strong* acid with a *strong* base, the ionization of the water is *so small compared to that* of the acid, the base, and the salt that is

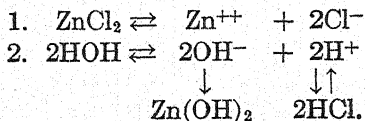
also formed, that its effect is negligible. But when we try to neutralize a strong base with a weak acid, then the effect of the *slight* ionization of the water compared to the rather feeble ionization of the weak acid must not be neglected. Its tendency to counteract the effects of neutralization is shown by the action of water in the decomposition of some salts by what is called *hydrolysis*. When sodium chloride is dissolved in water, there is almost *no hydrolysis*, because it is the salt of a *strong acid* and a *strong base*.

If we dissolve some sodium carbonate in water, and test the water solution with litmus as an indicator, we find that it *turns red litmus blue*. The solution of this salt, in other words, acts like a base. We may represent the equation as follows:



The ionization of the water as shown in equation No. 2 supplies some hydroxyl ions that combine with the sodium ions from ionic equation No. 1 to form some sodium hydroxide, strongly dissociated. The hydrogen ions from the water unite with the carbonate ion to form undissociated molecules of the weak carbonic acid. Hence, *a salt formed from a strong base and a weak acid will hydrolyze in water, and the solution will act as a base.*

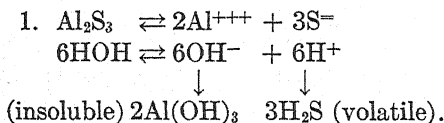
If we dissolve zinc chloride in water, the solution will turn blue litmus red. Zinc chloride is the salt of a *strong acid*, hydrochloric, and of a *weak base*, zinc hydroxide. Let us write the ionic equations:



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The hydrogen ion from the water gives the acid reaction for the strongly ionized hydrochloric acid. Undissociated molecules of zinc hydroxide are formed from the zinc ion and the hydroxyl ion of the water. Hence, *a salt formed from a strong acid and a weak base hydrolyzes in water, and the solution acts like an acid.*

The salt of a very weak base and a very weak acid hydrolyzes almost completely. The following reaction occurs when we add water to aluminum sulfide:



The aluminum hydroxide is little soluble and hence non-ionized; the hydrogen sulfide is volatile and escapes as a gas. Hence we have both a precipitate formed and a volatile product, and the reaction runs practically to completion. *The salt formed from a very weak base and a very weak acid hydrolyzes almost completely.*

### SUMMARY

*Equilibrium* in a chemical reaction is established when the speed at which the factors combine to form products is just equaled by the speed at which such products recombine to form the original factors. Equilibrium is *dynamic*, instead of *static*.

In physical equilibrium, we may have equilibrium between dissolved molecules of solute and the undissolved mass. Equilibrium between undissociated molecules and dissociated molecules is ionic equilibrium. Chemical reactions sometimes run to equilibrium.

Reactions run to completion normally: (1) *If an insoluble compound is formed as one of the products;* (2) *If a volatile product is set free;* (3) *If a compound is formed that does not ionize, such as water.* The first two statements were first formulated by Berthollet. Hence they are called Berthollet's Laws.

It is possible for a chemist to displace an equilibrium reaction: (1) *by a temperature change*; (2) *by a pressure change*; (3) *by changing both temperature and pressure, either with or without the presence of a catalyst*; (4) *by changing the concentration*.

The Law of Mass Action, or the Law of Molecular Concentration, may be briefly summarized as follows: *The speed of a reaction is proportional to the products of the concentrations of the reacting substances*. It was formulated by Guldberg and Waage.

*Hydrolysis* is that interaction of water with a salt that causes its decomposition or partial decomposition. It is the reversal of neutralization.

If both the acid and the base that form a salt are very strong, the salt does not hydrolyze. A salt formed from a strong acid and a weak base hydrolyzes, and acts like an acid. A salt formed by a strong base and a weak acid hydrolyzes, and acts like a base. Practically complete hydrolysis occurs when water is added to the salt formed by a very weak base and a very weak acid.

## QUESTIONS

1. Make a list of 20 equations from those we have studied and explain why they run to completion or to equilibrium, whichever the case may be.

2. Select five equilibrium equations that we have studied, and tell how you could drive the reaction more nearly to completion in one direction.

3. Why do you think that physical chemistry has become so important in college chemistry courses?

4. Study the formulas for the following salts. Tell which ones you would expect to hydrolyze, and how the solution would react toward litmus:  $\text{KCl}$ ;  $\text{K}_2\text{CO}_3$ ;  $\text{FeCl}_3$ ;  $\text{ZnSO}_4$ ;  $\text{Na}_2\text{SO}_4$ ;  $\text{CuCl}_2$ ;  $\text{CuSO}_4$ ; and  $\text{AlCl}_3$ .

5. Suppose you are dissolving stannous chloride in water, and a precipitate of stannous hydroxide forms by hydrolysis. Would the addition of hydrochloric acid increase or decrease the hydrolysis? Explain.

6. If a certain dye is the sodium salt of a color acid, would the

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addition of sodium sulfate to a water solution of the dye make it less soluble? Explain.

7. A water solution of lead acetate is usually somewhat cloudy. What should you add to the solution to make it transparent?

8. Explain why washing soda,  $\text{Na}_2\text{CO}_3$ , is a good cleansing agent.

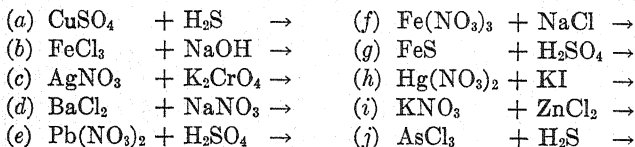
9. Under what conditions do double decomposition reactions run to completion?

10. What do you think would be the effect of heating calcium carbonate in a sealed tube? Explain.

11. Is it correct to think of water as having to a slight degree both the properties of an acid and of a base?

12. Name several ways in which the equilibrium point of a chemical reaction may be shifted.

13. Complete each of the following equations, indicating whether they run to completion or to equilibrium: (Before you try to write the equations, look up in Table 4 in the Appendix the solubility of the products you would expect to have formed.)



14. Which of the following compounds can be made by double decomposition? (See solubility table.)  $\text{CuSO}_4$ ;  $\text{PbSO}_4$ ;  $\text{PbCrO}_4$ ;  $\text{CdS}$ ;  $\text{AlCl}_3$ ;  $\text{Zn}(\text{OH})_2$ ;  $\text{HgCl}_2$ ;  $\text{CaCO}_3$ ;  $\text{NaNO}_3$ ;  $\text{Ag}_2\text{S}$ . In three cases, explain how you would proceed.

## CHAPTER 23

### SULFUR AND SULFIDES

#### Vocabulary

**Mobile.** Capable of moving freely; referring to liquids that flow easily.

**Viscous.** Thick; not mobile.

**Octahedron.** An eight-sided geometrical figure.

**Monoclinic.** An axis of a crystal is an imaginary line between the centers of opposite faces; if one axis is inclined to the others, the crystal is monoclinic.

**Rhombic.** Having the form of a rhombus.

**Prismatic.** Shaped like a prism.

#### A. SULFUR

**303. Where Sulfur Is Found.** We naturally associate sulfur with volcanic regions. It is found in Popocatepetl, a volcano in Mexico. Sicily has long been a source of sulfur. This element occurs in widely distributed areas, either free, or uncombined, or in such compounds as sulfides or sulfates. At the present time enormous quantities of sulfur are produced in Louisiana and Texas; the bulk of the supply now comes from the latter state.

**304. How a Mining Problem Was Solved.** The sulfur beds in Texas and Louisiana lie at a depth of 500 ft., or more, and in some places they are 200 ft. thick. But these beds are covered with quicksand, and a hole dug in quicksand is only a little more permanent than a hole dug in water. Hence several attempts to sink a mining shaft down to the sulfur beds resulted in failure.

Herman Frasch, an American chemist, devised the following scheme for getting the sulfur. As a casing, a 12-in. iron



pipe was driven down to the sulfur beds. Inside this casing, there are three concentric pipes, 6 in., 3 in., and 1 in. in diameter respectively. They extend down into the sulfur beds beneath. (See Fig. 193.) Into the outer pipe *superheated* water at a pressure of 100 lb. per sq. in. is forced. Under

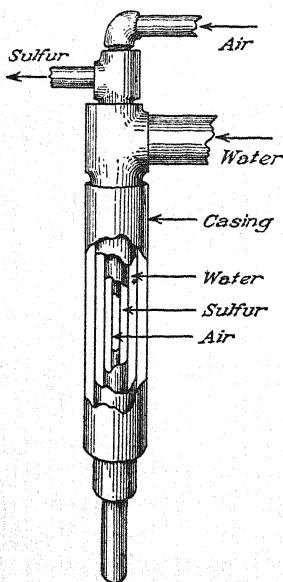


FIG. 193. — Pipes as used in Frasch process.

this pressure, the water is hot enough to melt the sulfur. Hot compressed air, which is forced down the inner pipe, mixes with the melted sulfur and decreases its density. The joint pressure of the hot air and the superheated water is sufficient to push the melted sulfur up through the middle pipe. (See Fig. 194.) The molten sulfur flows into wooden bins that may measure 20 ft. in width, from 30 to 50 ft. in height, and 100 ft. in length. After the sulfur has solidified, the sides of the bin are removed, the huge block of sulfur is broken up by blasting, and it is then loaded on freight cars by means of steam shovels. Figure 195 shows

a large block of sulfur that was mined by the *Frasch process*.

**305. How Sulfur Is Purified.** The sulfur obtained from Texas and Louisiana is so pure that for ordinary commercial purposes no further purification is necessary. Its purity is about 99%. If further purification must be done, the sulfur is distilled in earthenware retorts. The vapor condenses on the walls and on the floor of a large brick chamber. The fine powder is called *flowers of sulfur*. The sulfur that condenses on the floor of the chamber is usually drawn off as a liquid

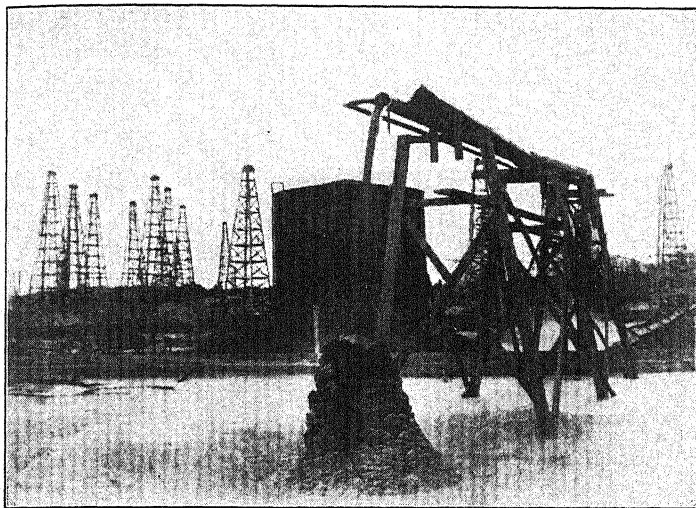


FIG. 194. — Stream of molten sulfur issuing from a sulfur well.

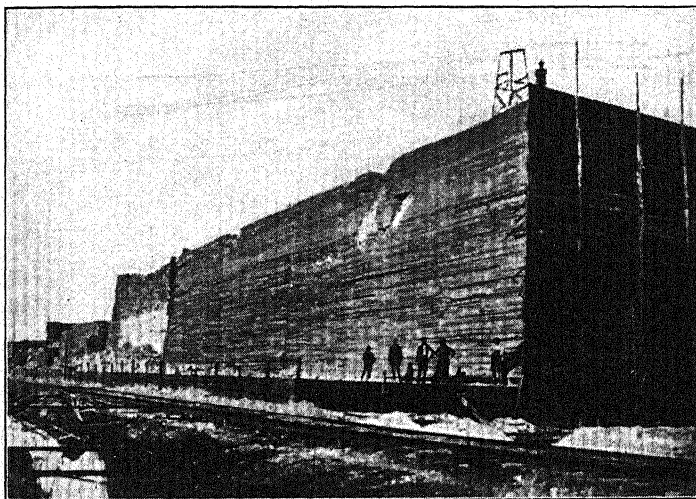


FIG. 195. — A block of Louisiana sulfur.

to solidify in molds. The product is called *roll sulfur*, or *brimstone*.

**306. Physical Properties of Sulfur.** Ordinary sulfur is a yellow crystalline solid. It is practically insoluble in water, but it dissolves readily in carbon disulfide and in some bases. When an acid is added to a solution of sulfur in a base, the sulfur is precipitated as a fine white powder called *lac sulfur*, or *milk of sulfur*. The density of sulfur is about twice that of water. Sulfur melts at a temperature of  $114.5^{\circ}\text{C}$ ., forming a pale yellow, mobile liquid. When it is heated still higher, instead of becoming more mobile as liquids usually do, it becomes more viscous. At a temperature of about  $250^{\circ}\text{C}$ . the melted sulfur becomes so thick that it hardly flows from an inverted tube. As the temperature rises, the color changes from a light yellow to a brown or reddish brown, and then almost to black. At a still higher temperature, the fluidity increases again and the liquid flows freely. It boils at  $445^{\circ}\text{C}$ . All of the general properties of sulfur do not apply to all the various allotropic forms of sulfur. Each one has some distinct properties.

**307. The Allotropic Forms of Sulfur.** 1. *Rhombic sulfur*. If we dissolve a little brimstone in some carbon disulfide, and then let the disulfide evaporate, crystals of sulfur will separate from the solution. The crystals that are formed in this way will be shaped like an octahedron. (See Fig. 196.) Such crystals are stable at room temperature. They are a little more than twice as dense as water.

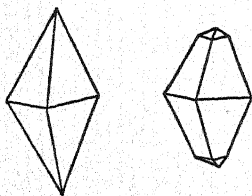


FIG. 196.—Rhombic sulfur crystals.

2. *Prismatic sulfur*. Let us melt some sulfur in a large crucible, cool it slowly until a crust forms, break the crust and pour off the excess liquid; the interior of the crucible will be lined with a mass of pointed, needle-like crystals of

prismatic sulfur. (See Fig. 197.) These crystals belong to the *monoclinic* system of crystallization. Sulfur crystallizes in the monoclinic, or prismatic, form when it solidifies from

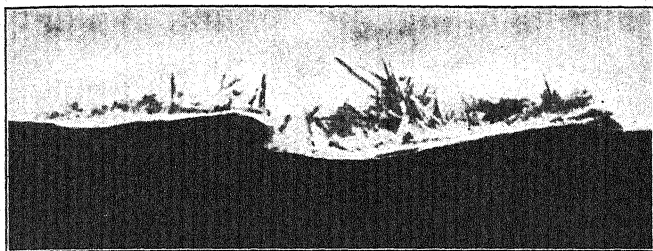


FIG. 197. — Needle-like crystals of prismatic sulfur.

the molten state. Monoclinic sulfur is not quite twice as dense as water. If it is cooled below  $96^{\circ}\text{C}.$ , it gradually changes into the rhombic form.

3. *Amorphous sulfur*. If we boil some sulfur in a retort, as shown in Fig. 198, and let the boiling sulfur flow into cold water, we get a rubbery, plastic form of sulfur. It does not crystallize at all. Its color is dark brown. In fact one inexperienced with this form would not recognize it as sulfur at all. Amorphous sulfur is insoluble in ordinary reagents. When it stands at room temperature, it gradually changes to the rhombic form. Here, again, we find that an element may exist in different allotropic forms. A gain in energy produces either the monoclinic or the plastic form, but a recurrence to the rhombic form occurs at lower temperatures.

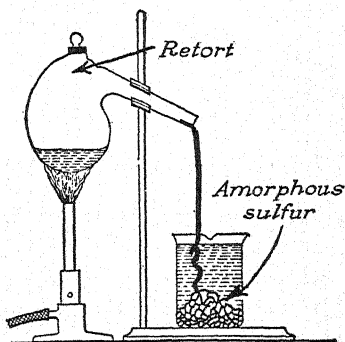
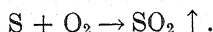


FIG. 198. — Amorphous sulfur.

**308. Chemical Properties of Sulfur.** At ordinary temperature sulfur is not very active. When heated, it unites with oxygen, burning with a blue flame and forming sulfur dioxide:



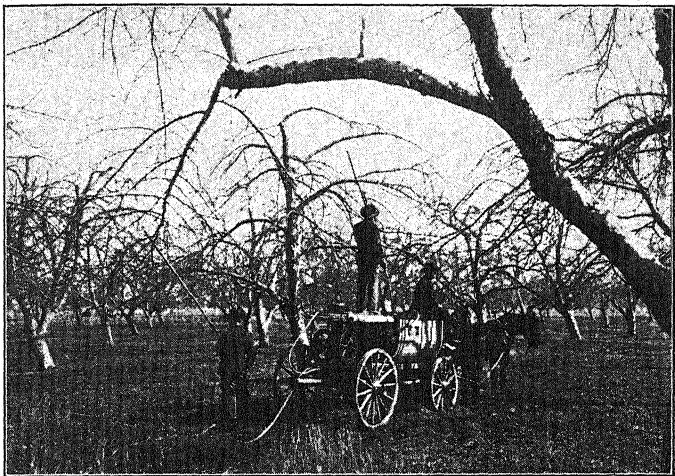
Traces of sulfur trioxide,  $\text{SO}_3$ , are formed when sulfur burns. Sulfur can be made to combine with hydrogen, carbon, chlorine, and other non-metals. Such compounds, however, are formed with some difficulty, and they are not very stable. From the formulas  $\text{SO}_3$ ,  $\text{SO}_2$ , and  $\text{H}_2\text{S}$ , it is apparent that sulfur may have the following valences: + 6, + 4, or - 2. Sulfur is similar to oxygen in the manner in which it combines with metals. Powdered zinc and sulfur combined explosively. The heat produced when iron filings and powdered sulfur unite causes the mass to be heated to incandescence. Copper unites with the vapor from boiling sulfur. If the oxide of a metal is insoluble, generally the sulfide of that metal is insoluble. The following table shows a chemical similarity between oxygen and sulfur:

Hydrogen sulfide.....	$\text{H}_2\text{S}$	Hydrogen oxide.....	$\text{H}_2\text{O}$
Carbon disulfide.....	$\text{CS}_2$	Carbon dioxide.....	$\text{CO}_2$
Copper sulfide.....	$\text{CuS}$	Copper oxide.....	$\text{CuO}$
Zinc sulfide.....	$\text{ZnS}$	Zinc oxide.....	$\text{ZnO}$
Mercuric sulfide.....	$\text{HgS}$	Mercuric oxide.....	$\text{HgO}$

**309. Uses of Sulfur.** This element finds use in making sulfur dioxide, carbon disulfide, sulfuric acid, and other compounds of sulfur. Several million tons are used annually in the making of sulfuric acid. Matches, fireworks, and black gunpowder all contain sulfur or sulfur compounds. The sulfur dyes find use in dyeing hosiery. They form fast black dyes.

It was in 1839 that Charles Goodyear, an American inventor, had the good fortune to spill on a hot stove a mix-

ture of rubber and sulfur with which he was experimenting. The product that was formed was the forerunner of the *vulcanized rubber* that makes modern rubber tires and rubber products possible. Without sulfur, the rubber that was smeared on fabric to make water-proof "gum boots" was "gummy" in hot weather and brittle in cold weather. The vulcanized product is elastic and impervious, and not affected



Courtesy of U.S. Dept. of Agriculture

FIG. 199. — A spraying machine used with lime-sulfur.

so much by temperature changes. The hardness of vulcanized rubber depends upon the temperature at which the vulcanizing is done, and upon the per cent of sulfur that is added. Rubber bands, rubber stoppers, and rubber tubing contain small quantities of sulfur. Hard rubber contains a larger quantity.

A mixture of four parts of powdered sulfur with one part of arsenate of lead makes an excellent fungicide. It finds use in destroying mildew and blight on roses and other plants. When sulfur is boiled with lime and water, it forms a

red liquid which consists essentially of poly-sulfides of calcium,  $\text{CaS}_x$ , for example. This *lime-sulfur solution* is extensively used for spraying fruit trees to destroy scale insects and as a fungicide. (See Fig. 199.)

## B. HYDROGEN SULFIDE

**310. Sources of Hydrogen Sulfide.** All protein material contains some sulfur. When such protein material decays, small quantities of hydrogen sulfide are formed. The odor from decayed eggs is due to the presence of this gas. Coal is seldom free from sulfur. When coal burns, traces of hydrogen sulfide and sulfur dioxide get into the air. The tarnishing of silverware is due to the action of hydrogen sulfide in forming a metallic sulfide with the silver.

**311. How Hydrogen Sulfide Is Prepared.** When hydrogen is bubbled through molten sulfur, some hydrogen sulfide is formed. The reaction is reversible, however, and not practical for the preparation of hydrogen sulfide in any considerable quantity.

In the laboratory, hydrogen sulfide is usually prepared by the action of hydrochloric acid or dilute sulfuric acid on the sulfide of a metal. Iron sulfide and hydrochloric acid interact as shown:

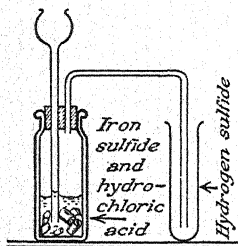
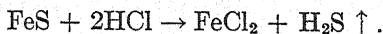


FIG. 200. — Laboratory apparatus for making hydrogen sulfide.



In this double decomposition reaction, the hydrogen sulfide is volatile and the reaction runs to completion. The gas is usually collected by air displacement. (See Fig. 200.)

**312. Physical Properties of Hydrogen Sulfide.** The gas is colorless, and it has the disagreeable odor of rotten eggs. It is heavier than air, and moderately soluble in water. The gas is poisonous when inhaled. In concentrated form, it is a violent

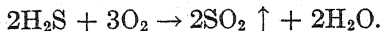


poison; when diluted with air, it causes nausea, headache, and dizziness.

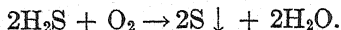
**313. How Hydrogen Sulfide Acts Chemically.** The chemical behavior of hydrogen sulfide can be studied conveniently under the following sub-topics:

1. *As an acid.* When hydrogen sulfide is dissolved in water, it can neutralize bases, turn blue litmus red, and form salts. Such a solution is called *hydrosulfuric acid*. It does not ionize largely; hence it is a weak acid.

2. *Hydrogen sulfide burns.* Since both of the constituents of hydrogen sulfide combine with oxygen readily, we may expect the gas to burn, too. When it burns, the products that are formed will depend upon the relative amount of oxygen present. If there is sufficient oxygen to combine with all the hydrogen and all the sulfur, the products formed are sulfur dioxide and water.



If there is not enough oxygen to combine with both elements, then the hydrogen will unite with the oxygen present, and sulfur will be set free.

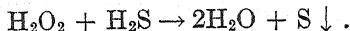


It is possible, too, to have just enough oxygen present to unite with all the hydrogen, and to burn *part* of the sulfur. When a solution of hydrogen sulfide is exposed to the air, slow oxidation occurs; the hydrogen is oxidized, and sulfur is precipitated. The student should compare the burning of hydrogen sulfide in varying proportions of air with the burning of hydrocarbons under similar conditions.

3. *As a reducing agent.* Hydrogen sulfide is not very stable; it decomposes into hydrogen and sulfur, two elements that have a strong affinity for oxygen. Therefore, hydrogen sulfide is a good reducing agent. If we bubble the gas through a solution of hydrogen peroxide, the peroxide will

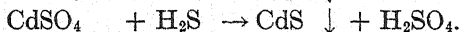
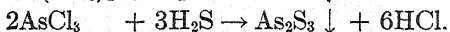
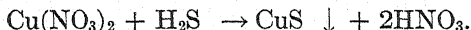


be reduced to water; sulfur is precipitated as a fine white powder. The equation follows:



4. *Hydrogen sulfide acts on metals.* The water solution of hydrogen sulfide attacks metals and forms sulfides. Organic substances, such as eggs, mustard, etc., contain considerable sulfur. As they decompose, hydrogen sulfide is formed. A silver spoon left in contact with such food soon becomes covered with a coating of silver sulfide. The tarnishing of some other metals is due to the formation of sulfides.

**314. Uses of Hydrogen Sulfide.** In qualitative analysis hydrogen sulfide is extensively used as a reagent. The sulfides of many metals are insoluble. When hydrogen sulfide is added to a solution containing such metals, the insoluble sulfides that are formed are thrown out of solution as precipitates. The equations represent typical examples:

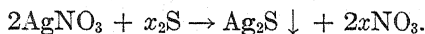


If the hydrogen sulfide is added to a solution containing several metals, their sulfides will all be precipitated together. In *qualitative analysis*, the student learns how to separate the sulfides from one another and to identify each one. Carefully worked out schemes of analysis are based to a large extent upon the solubilities of the sulfides of different metals in different reagents. For example, the sulfides of zinc and manganese are soluble in dilute acids; the sulfides of arsenic and tin are soluble in ammonium sulfide; the sulfides of copper and lead are soluble in hot dilute nitric acid, but the sulfide of mercury is insoluble.

**315. Sulfur Springs.** Some natural springs and some artesian wells contain hydrogen sulfide in solution. This gas

gives to such water its disagreeable odor and peculiar taste. The water from some sulfur springs is claimed to have certain medicinal properties. Sulfur is deposited as the hydrogen sulfide oxidizes upon contact with the air.

**316. Test for Sulfide Ions.** In water solution, hydrogen sulfide, or any soluble sulfide, furnishes *sulfide ions*,  $S^{=}$ . These ions will unite with such metals as silver, lead, or copper to form precipitates. The sulfides of the three metals named are black; arsenic and cadmium form yellow sulfides; antimony sulfide is orange in color. To test for a soluble sulfide, then, we may add to the unknown solution a few drops of silver nitrate solution. If a sulfide is present, a *black* precipitate of silver sulfide will be formed.



The letter  $x$  represents either hydrogen or some metal.

### C. OTHER SULFIDES

★ **317. Metallic Sulfides.** Many of the important ores found in nature are sulfides. Large quantities of copper sulfide are found in Montana; zinc sulfide is one of the important ores of zinc; lead sulfide is the most common ore of lead; sulfides of silver, tin, nickel, arsenic, and iron are also found in nature.

★ **318. Carbon Disulfide,  $CS_2$ .** When sulfur vapor is passed over charcoal heated in an electric furnace, a nearly colorless liquid is formed. It is a disulfide of carbon, analogous to the dioxide of carbon. The commercial product has a disagreeable odor. It does not mix with water. The liquid is volatile, and its vapor burns explosively.



When this liquid is poured into the holes of small burrowing rodents, such as gophers, rats, and mice, and then

ignited, the heavy products of combustion soon settle down to the animals underground, and suffocate them. Hence this liquid finds use in destroying pests and as an insecticide. It is a good solvent for rubber, phosphorus, waxes, and resins. A solution of rubber in carbon disulfide is used as a rubber cement.

### SUMMARY

Sulfur occurs in volcanic regions. It is believed that beds of sulfur are sometimes formed by the decomposition of sulfates in the presence of bacteria. Rich deposits of sulfur are found in Louisiana and Texas.

*Crude* sulfur is purified by *distillation*. It is sold as *flowers of sulfur*, *roll sulfur*, and *lac sulfur*.

Sulfur exists in three solid allotropic forms: *rhombic* sulfur, *prismatic* sulfur, and *amorphous* sulfur. Sulfur is about twice as heavy as water; it is *insoluble* in water but dissolves readily in carbon disulfide.

Sulfur burns with a pale blue flame forming sulfur dioxide. It unites readily at higher temperatures with most metals.

Hydrogen sulfide is prepared by the action of an acid on a sulfide. It is a colorless gas with a very disagreeable odor. The gas is heavier than air and soluble in water.

Hydrogen sulfide burns with a blue flame. It is a reducing agent. *In water solution it acts like an acid* and it combines with metals to form sulfides. It is used in qualitative analysis.

*Carbon disulfide* is an oily liquid; it burns readily. It is used as a solvent, and as a germicide and insecticide.

### QUESTIONS

#### GROUP A

1. Write three equations for the burning of hydrogen sulfide, varying the amount of oxygen used.
2. Why does silverware tarnish so readily in city dwellings?
3. How do you account for the unpleasant odor and taste of certain springs?

4. Why does a rubber band stretched over a silver coin soon form a brown mark or stain?
5. Why do we call a solution of hydrogen sulfide a weak acid? Do you think such a solution would be a good conductor?
6. Why is carbon monoxide a more dangerous poison than hydrogen sulfide?
7. Iron pyrites, or "fool's gold," has the formula  $\text{FeS}_2$ . How would you prove that it is not gold?
8. If you were given a yellow powder, how could you prove that it contains nothing but sulfur?
9. Make a list of the applications of sulfur.
10. What is meant by vulcanization of rubber? Why is the process so important?

## GROUP B

11. Devise a method of testing for traces of hydrogen sulfide.
12. Lead sulfide is black. Would you recommend the use of white lead for painting the walls and ceiling of a chemical laboratory? Explain.
13. Write the equations to show the reaction of hydrogen sulfide with the chlorides of mercury, antimony, zinc, nickel, and bismuth. In which one of these reactions will no precipitate be formed, and why?
14. Write equations to show three methods of preparing copper sulfide.
15. Why cannot nitric acid be used in preparing hydrogen sulfide?
16. When hydrogen sulfide is added to a solution of zinc chloride, the reaction runs to equilibrium. What could you add to the solution to decrease the concentration of the hydrogen ion and make the reaction go to completion?
17. How could you make hydrogen sulfide, if you had as materials iron, sulfur, and hydrochloric acid?
18. From the formula for carbon disulfide, would you expect the liquid to burn? Explain.
19. Write ionic equations to show the reaction of hydrogen sulfide on the solutions of lead nitrate and silver nitrate.
20. Explain why hydrogen sulfide solutions are kept in brown bottles?

## PROBLEMS

## GROUP A

1. How many grams of iron sulfide must be used to prepare 100 grams of hydrogen sulfide?
2. If hydrogen chloride is used with the iron sulfide in Problem 1, how many grams of HCl are needed?
3. How many grams of ferrous chloride are left in the solution after the reaction is finished?
4. How many pounds of sulfur must be used to make 400 lb. of copper sulfide?

## GROUP B

5. Calculate the weight of 500 c.c. of hydrogen sulfide at S. T. P.
6. How many liters of air must be used to burn completely 40 liters of hydrogen sulfide? How many liters of sulfur dioxide are formed?
7. How many liters of carbon dioxide are formed by burning 380 gm. of carbon disulfide? How many liters of sulfur dioxide are formed at the same time?
8. From the formula for hydrogen sulfide, calculate its specific weight, air standard.

## CHAPTER 24

### OXIDES AND ACIDS OF SULFUR

#### Vocabulary

**Roasting.** The heating of ores in the presence of air.

**Antiseptic** (against decay). A substance that destroys putrefactive bacteria. It may be used upon a living body.

**Disinfectant.** A substance that may be applied to objects to destroy bacteria. Some disinfectants are too active to be applied to living tissues.

**Di-basic.** Referring to an acid that has two replaceable hydrogen atoms per molecule.

**Thio.** A prefix meaning *sulfur*. Used to refer to compounds in which sulfur atoms have been substituted for oxygen atoms.

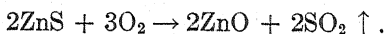
#### A. OXIDES OF SULFUR

**319. The Oxides of Sulfur.** In our study of the properties of sulfur, we learned that two oxides of sulfur are possible. Sulfur dioxide has the formula  $\text{SO}_2$ ; sulfur trioxide has the formula  $\text{SO}_3$ . Sulfur dioxide finds its way into the air from smelters where sulfide ores are roasted. Coal usually contains some sulfur. Hence sulfur dioxide is formed by burning such coal.

**320. How Sulfur Dioxide Is Prepared.** 1. *By burning sulfur.* If the sulfur dioxide is to be used for some purpose where the nitrogen and other elements in the air are not objectionable, then the burning of sulfur is a good method of preparing it. The method is not satisfactory if reasonably pure sulfur dioxide is needed.

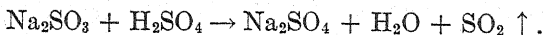
2. *By roasting sulfides.* We know that many ores occur as sulfides. Before the metal is extracted from such ores, they are roasted (heated in air) to get rid of the sulfur. The reaction with the sulfide of zinc is typical of the chemical

behavior, although the oxide of the metal is not always formed:



This method is used extensively in preparing sulfur dioxide for use in the manufacture of sulfuric acid. Iron pyrites,  $\text{FeS}_2$ , is the ore used.

3. *Decomposition of sulfites.* Pure sulfur dioxide may be prepared by the action of an acid on a sulfite. Sodium sulfite,  $\text{Na}_2\text{SO}_3$ , treated with sulfuric acid reacts as shown in the following equation:



It is probable that sulfurous acid,  $\text{H}_2\text{SO}_3$ , is first formed, and that it decomposes into water and sulfur dioxide.

(See Fig. 201.)

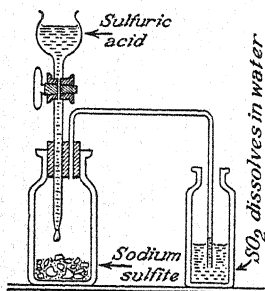
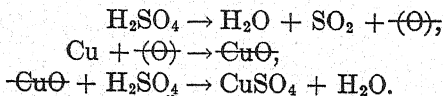


FIG. 201.—Laboratory preparation of sulfur dioxide.

4. *By the reduction of sulfuric acid.* Hot, concentrated sulfuric acid is a vigorous oxidizing agent. When a metal is treated with the hot acid, a series of reactions probably takes place. The acid liberates oxygen which attacks the metal, and sulfur dioxide and water are formed as decomposition products of the acid. The excess acid converts the oxide of the metal into the

sulfate. Let us write a series of equations to show the possible steps in the reaction:

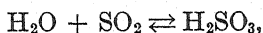


If we cancel the factors and products that are common to both sides of the equations, we may then combine the *partial* equations into the following *final* equation:



**321. Physical Properties.** Pure sulfur dioxide is a colorless gas; it has a choking, suffocating odor. As prepared in the laboratory, it has a whitish appearance due to the presence of traces of sulfur trioxide. Sulfur dioxide is more than twice as heavy as air; it is very soluble in water. It is one of the easiest gases to liquefy, since it will liquefy at room temperature under a pressure of about two atmospheres. Liquid sulfur dioxide is sold in steel containers.

**322. How Sulfur Dioxide Behaves Chemically.** 1. *As an acid.* Sulfur dioxide is the *anhydride of sulfurous acid*. When it dissolves in water,



it forms a weak acid that will turn blue litmus red, or neutralize bases and form *sulfites*. The reaction is reversible. If the solution is heated, the acid decomposes into water and sulfur dioxide. When the solution stands exposed to air, it takes on oxygen and forms sulfuric acid.

2. *Its activity.* Sulfur dioxide neither burns nor supports combustion. By the use of a suitable catalyst, or by the use of an oxidizing agent, it may be oxidized to sulfur trioxide. Thus it acts as a reducing agent. The valence of the sulfur is increased from a + 4 to a + 6. ( $\text{SO}_2 + (\text{O}) \rightarrow \text{SO}_3$ .) Since sulfur can also have a valence of - 2, sulfur dioxide may sometimes act as an oxidizing agent. If treated with hydrogen, it may oxidize the hydrogen and form water and hydrogen sulfide. Thus this gas may at times act as a reducing agent and under other conditions as an oxidizing agent. It is a fairly stable compound.

3. *As a bleaching agent.* Sulfur dioxide unites with the colored compounds of many organic substances and forms colorless compounds. For example, sulfur dioxide bleaches flowers, straw, etc., when they are moist. Some chemists



believe that the bleaching action of sulfur dioxide is due to its ability to act as a reducing agent.

**323. Uses of Sulfur Dioxide.** 1. *As a disinfectant and preservative.* As a rule, a chemical that will destroy disease-producing bacteria will also destroy the bacteria that cause decay. Hence a disinfectant is also a preservative. If that preservative is to be used in food-stuffs it should not be toxic to human beings. Sulfur dioxide is used as a disinfectant and as an insecticide. It is used sometimes in preserving foods,

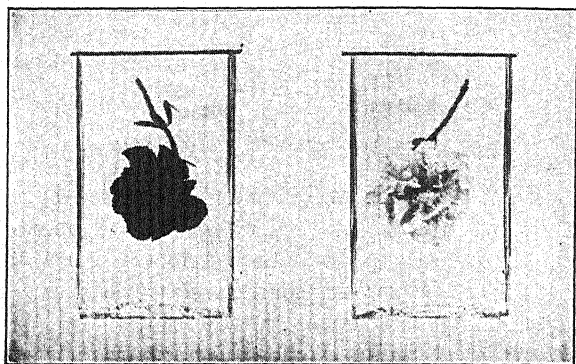


FIG. 202. — Carnations showing the bleaching effects of sulfur dioxide.

but such use is questionable. It has been used to bleach and preserve such foods as canned corn, sausage, and fruits.

2. *For bleaching.* Wool, straw, and silk are sometimes bleached with sulfur dioxide. It does not injure the fiber, but the bleach is not permanent. If a straw hat is bleached with sulfur dioxide, and then worn in sunlight for a few weeks, the yellow color reappears. Carnations lose their color rapidly, if placed in moist sulfur dioxide. (See Fig. 202.) It also finds use in bleaching flour, molasses, and dried fruits. Maraschino cherries are bleached with sulfur dioxide, and then dyed red or green by the use of a dye-stuff.

3. *As a refrigerant.* Nearly all household refrigerators

of the mechanical type use sulfur dioxide as the refrigerant. A small electric motor is used to compress the gas and liquefy it. The coils in which it is liquefied are cooled by currents of air flowing around them. Then the liquid

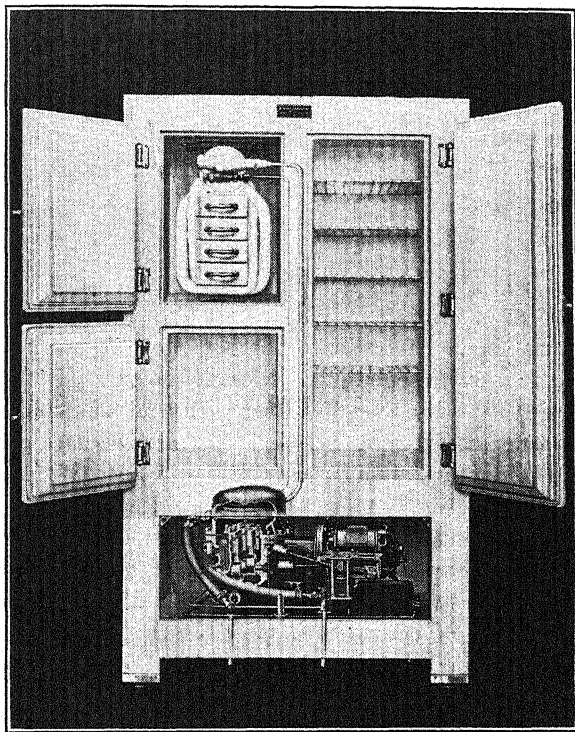


FIG. 203. — Sulfur dioxide is liquefied in the lower compartment. As it evaporates in the coils (upper left) it absorbs heat and freezes water in the shallow pans.

evaporates in coiled pipes which surround the trays that contain the water to be frozen. The heat needed to vaporize the sulfur dioxide comes from the air of the refrigerator, thus cooling it, and from the water, which loses so much heat that it freezes. (See Fig. 203.)

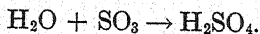
4. *For making sulfites and sulfuric acid.* Enormous quantities of sulfuric acid are made from sulfur dioxide. Since its water solution forms sulfurous acid, it may interact with bases to form *sulfites*.

**324. Sulfites.** Only a few of the sulfites are used very extensively. Since sulfurous acid ionizes in two stages, it may form the acid sulfite ion,  $\text{HSO}_3^-$ , as well as the sulfite ion,  $\text{SO}_3^{=}$ . The sulfites and the bi-sulfites of sodium and potassium are water soluble compounds. *Calcium bi-sulfite*,  $\text{Ca}(\text{HSO}_3)_2$ , is used extensively in treating wood pulp in the paper industry.

### B. SULFUR TRIOXIDE AND SULFURIC ACID

**325. Sulfur Trioxide.** This compound is the anhydride of sulfuric acid. At ordinary temperatures it is a colorless liquid. In the presence of a trace of moisture, it forms a white solid that dissolves in water with a hissing sound. It is a vigorous oxidizing agent. It is the intermediate product in the manufacture of sulfuric acid.

**326. How Sulfuric Acid Is Made.** Since sulfuric acid is used in preparing many other acids, no doubt the student has wondered how sulfuric acid is manufactured. He will learn that it is important to use sulfuric acid to make more sulfuric acid. Of course it is possible to prepare sulfuric acid by dissolving its anhydride,  $\text{SO}_3$ , in water.

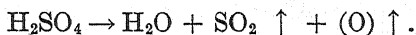


But the problem the manufacturer has to solve is to make the sulfur trioxide in quantity. In the *contact process*, a catalyst is used to convert sulfur dioxide into sulfur trioxide. In the *chamber process*, sulfur dioxide is oxidized to the trioxide by the use of the oxides of nitrogen. Nitric oxide, for example, serves as a "carrier"; it takes on oxygen from the air, and gives it up to the sulfur dioxide.

**327. Physical Properties of Sulfuric Acid.** Sulfuric acid is a heavy, oily liquid; it is frequently called "oil of vitriol." Ordinary concentrated sulfuric contains about 93.5% acid; its specific weight is from 1.83 to 1.84. The boiling point of this acid is higher than that of most common acids, about 338° C. Pure sulfuric acid is colorless but the commercial acid is often colored yellow to almost black due to impurities, especially organic matter. When sulfuric acid is added to water, a great deal of heat is evolved. The action is chemical, since hydrates of sulfuric acid,  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , or  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , are formed. These hydrates decompose when the acid solution is heated. Sulfuric acid burns the flesh frightfully, and great care must be used not to let it come into contact with the skin.

**328. Chemical Behavior of Sulfuric Acid.** 1. *Acid action.* Dilute sulfuric acid has all the properties that are characteristic of typical acids. It acts on metals, the oxides of metals, and neutralizes bases forming *sulfates*.

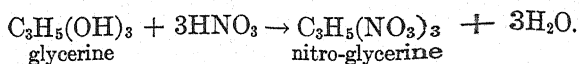
2. *As an oxidizing agent.* When sulfuric acid is heated it decomposes into water, sulfur dioxide, and oxygen.



The nascent oxygen is a vigorous oxidizing agent. Thus *hot concentrated* sulfuric acid acts as an oxidizing agent in a manner similar to hot nitric acid, although it is not so vigorous. The action of hot concentrated sulfuric acid on copper, as shown in Section 320, is typical of its behavior. The *cold, dilute sulfuric acid* interacts with *active* metals and liberates hydrogen.

3. *As a dehydrating agent.* Sulfuric acid is very greedy for water. Gases may be dried by bubbling them through concentrated sulfuric acid. In fact, the affinity of this acid for water is so great that it will take hydrogen and oxygen, in the proportion needed to form water, from such substances as sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ), cellulose,  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , etc., and leave the

carbon uncombined. In this manner **sulfuric** acid chars wood, paper, cotton, sugar, and other **organic** compounds. If the acid is heated with such substances for some time, it will oxidize the carbon, too, and form **carbon** dioxide. In many industries where the chemical reaction forms water, **sulfuric** acid is used to take up the water as fast as it is formed and thus prevent the dilution of the **other** chemicals. The reaction for the manufacture of **nitro-glycerine** may be used to illustrate this type of reaction.

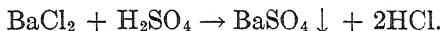


In making this explosive, a mixture of the concentrated acids, nitric and sulfuric, is used. The **nitric** acid interacts as represented in the equation, and the **sulfuric** acid takes up the water as fast as it is formed. Otherwise the nitric acid would soon become so dilute the action would stop. In many industries, sulfuric acid is used as a dehydrating agent.

**329. Uses of Sulfuric Acid.** To mention all the uses of sulfuric acid would require a long chapter, and it would necessitate naming nearly all the industries. So general is the use of this chemical that the following statement is often made: "The civilization of a country is measured by the amount of sulfuric acid it uses." Several million tons are made annually in the United States. In the explosives industry large quantities are used. Still larger quantities are used in making commercial fertilizers. In refining petroleum, sulfuric acid is used to char certain organic impurities. In cleaning metals, making sulfates, and in the preparation of acids, large quantities of this acid are used. From the preceding paragraphs we find that this acid is used quite extensively in its own preparation. It is not astonishing that Ellwood Hendrick calls sulfuric acid the "old horse" of chemical industry.

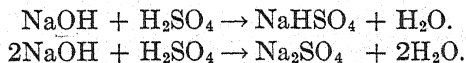
**330. Sulfates.** The sulfates form a very important class of salts. These salts are popularly known as *vitriols*. Copper sulfate is commonly called blue vitriol; zinc sulfate, white vitriol; and ferrous sulfate, green vitriol. Nearly all sulfates are soluble, the sulfates of lead, calcium, barium, and strontium being the chief exceptions.

**331. How to Test for a Sulfate.** When a solution of barium chloride is added to a solution containing sulfuric acid, or any soluble sulfate, a white precipitate of barium sulfate is formed.



This precipitate is insoluble in hydrochloric acid. Therefore, in testing a solution to see whether it contains a sulfate, we first add a little hydrochloric acid and then a solution of barium chloride. If a white precipitate forms, we know that the solution contained a sulfate.

**332. Sulfuric Acid May Form Two Kinds of Salts.** When we studied the ionization of acids, we learned that sulfuric acid may ionize to produce the  $\text{HSO}_4^-$  ion, or more completely to form the  $\text{SO}_4^{2-}$  ion. As a result, it may interact with metals or bases to form salts having either ion. For example,



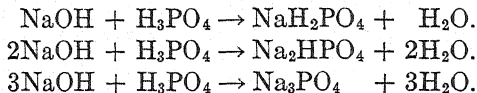
In the first case one atom of sodium replaces just one of the two hydrogen atoms of sulfuric acid and forms *sodium acid sulfate*,  $\text{NaHSO}_4$ . An *acid salt* always contains some of the hydrogen of the acid from which it was formed. Sodium acid sulfate is often called sodium *bi-sulfate*. *An acid like sulfuric that has two replaceable hydrogen atoms per molecule is called a di-basic acid.* From the second equation we see that one mole of such an acid just neutralizes two moles of a base like sodium hydroxide. Thus the name *di-basic*.

From a study of the second equation, we see that complete

neutralization of the sulfuric acid forms sodium sulfate,  $\text{Na}_2\text{SO}_4$ , a *normal* salt. Such salts are often called *neutral* salts, an unfortunate name since many of them act as acids or bases in solution. (See hydrolysis, Section 302.)

A glance at the formulas for nitric acid and hydrochloric acid must convince us that they can form *normal salts only*, since they have only one hydrogen atom per molecule. Such acids are *mono-basic*. It is obvious that sulfuric acid can form just twice as many salts as either one of these acids.

Phosphoric acid,  $\text{H}_3\text{PO}_4$ , is a *tri-basic* acid; it has three *replaceable* hydrogen atoms in its molecule. It may form three different salts as represented by the following equations:



★ In the first case we have formed  $\text{NaH}_2\text{PO}_4$ , which is called *mono-sodium phosphate*, or *di-acid sodium phosphate*; the salt  $\text{Na}_2\text{HPO}_4$  is called *di-sodium phosphate*, or *sodium acid phosphate*; the third salt,  $\text{Na}_3\text{PO}_4$ , is *tri-sodium phosphate*, or *normal sodium phosphate*.

★ 333. **Other Acids of Sulfur.** Several other acids of sulfur are known. *Fuming sulfuric acid*,  $\text{H}_2\text{S}_2\text{O}_7$ , was used under the name *oleum* during the World War for making "smoke screens." It finds use in the dye industry. The sodium salt of *thio-sulfuric acid*,  $\text{H}_2\text{S}_2\text{O}_3$ , has the formula  $\text{Na}_2\text{S}_2\text{O}_3$ . Its correct name is *sodium thiosulfate*, but it is better known as "hypo," a salt used in photography. The prefix "*thio*" means that one or more atoms of sulfur have been substituted for oxygen, atom for atom.

### SUMMARY

Sulfur dioxide may be prepared: (1) *by burning sulfur*; (2) *by roasting a sulfide*; (3) *by decomposition of sulfites*; (4) *by reduction of sulfuric acid*.



*Sulfur dioxide* is a heavy, suffocating gas; it is easily liquefied; it is very soluble in water.

Chemically, sulfur dioxide acts as a reducing agent; it is stable. In water solution, it forms sulfurous acid, a weak acid.

Sulfur dioxide finds use as a germicide, a preservative, a bleaching agent, and in the preparation of sulfuric acid and sulfites. It is a disinfectant and antiseptic. It is the most important substance used for household refrigeration.

Sulfur trioxide is prepared by oxidizing sulfur dioxide, either by the use of the oxides of nitrogen, or by the use of platinum as a catalyst. It is the anhydride of sulfuric acid.

Sulfuric acid may be made by the contact process or the chamber process. It is a heavy, oily liquid that mixes with water in all proportions. When *dilute*, it acts as an acid; when *hot* and *concentrated*, it is a vigorous oxidizing agent and a *dehydrating* agent. There are few industries in which sulfuric acid is not used, directly or indirectly.

A *di-basic acid* has two replaceable atoms of hydrogen per molecule; it is capable of forming two classes of salts: *acid salts*, and *normal salts*.

## QUESTIONS

### GROUP A

1. How would you prepare sulfur dioxide for a laboratory experiment? Can the gas be collected by water displacement?
2. In diluting sulfuric acid, why *must* the acid be poured into the water, and never the reverse?
3. How would you test a solution to determine the presence of a sulfate?
4. How would you test for a sulfite? For a sulfide?
5. Newspapers and straw hats become "yellow with age." Explain why.
6. It is not uncommon to find a brown ring on a table or shelf where a bottle of concentrated sulfuric acid has been standing. Explain.
7. Of what value is a beaker partly full of sulfuric acid in the glass case of a chemical balance?



8. Why does boiling sulfuric acid produce such frightful burns?
9. Twenty c.c. of sulfuric acid are measured out in a graduated cylinder, and permitted to stand in the laboratory for a few weeks. Will the volume increase, decrease, or remain constant? Explain.
10. The use of sulfuric acid is so extensive that it has been called the "king of chemicals." How does it happen that it is not so well known as copper, iron, cement, etc.?

## GROUP B

11. Is it possible for sulfuric acid to form an acid salt with calcium hydroxide? If so, write the equation.
12. Cream of tartar is an acid salt, potassium acid tartrate. How do you account for its sour taste and its action as an acid in baking powders?
13. How many sodium salts can be formed by the action of sodium hydroxide with a tetra-basic acid, such as  $\text{H}_4\text{SiO}_4$ ?
14. What compound do you think would be formed if you heated a sulfate with powdered charcoal?
15. At least 100 lb. of sulfuric acid are made annually for every man, woman, and child in the United States. How do you use 100 lb. of sulfuric acid annually?
16. If one writes on a paper with concentrated sulfuric acid, and then holds the paper near a flame, the writing appears black. Explain.
17. List three properties of sulfur dioxide that show how the uses of a substance are related to its special properties.
18. What is meant by the principle of "counter currents" as used in chemistry?
19. What advantages over platinum does vanadium oxide have as a catalyst?
20. Why would it be inadvisable to ship nitric acid or sulfuric acid in the same car with miscellaneous freight?

## PROBLEMS

## GROUP A

1. How many pounds of sulfuric acid can be prepared from one ton of sulfur that is 98% pure?

2. How many pounds of ferrous sulfate can be made by the action of a slight excess of sulfuric acid on 400 lb. of iron?
3. How many pounds of sodium sulfite are needed to prepare 40 lb. of sulfur dioxide?

## GROUP B

4. Calculate the weight of one liter of sulfur dioxide. Find its specific weight, air standard.
5. How many liters of sulfur dioxide will be formed by the action of an excess of sulfuric acid on 120 gm. of sodium sulfite?
6. One hundred gm. of copper interact with 100 gm. of sulfuric acid. How many liters of sulfur dioxide are set free?
7. In making sulfuric acid by the chamber process, how many cu. ft. of nitrogen peroxide must be used to oxidize 2000 cu. ft. of sulfur dioxide?

## SUPPLEMENTARY PROJECTS

Prepare a report on one of the following topics:

1. Uses of sulfuric acid.

Reference: HENDRICK, E., *Everyman's Chemistry*. Harper.

2. Advantages and disadvantages of chemical preservatives in food.

References: ECCLES, *Food Preservatives, Their Advantages and Proper Use*.

WILEY, H. W., *Foods and their Adulterations*. Blakiston.

3. Industrial catalysts.

Reference: HOWE, H. E., *Chemistry in Industry*, Vol. II, Chap. I. Chemical Foundation, Inc.

## CHAPTER 25

### THE HALOGEN FAMILY

#### Vocabulary

**Halogen.** A salt producer.

**Toxic.** Poisonous.

**Sedative.** A drug or medicine used to quiet the nerves.

**Lachrymator.** A substance that causes the tear glands to secrete tears freely.

**Alleviate.** To lighten or lessen.

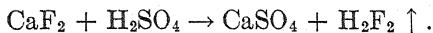
**334. The Halogen Family.** Four elements, fluorine, chlorine, bromine, and iodine are similar enough in their chemical behavior to be grouped by chemists in one *family* or *group*. Ellwood Hendrick calls it the "red-headed halogen family," because he has found that persons who have Titian-tinted locks are apt to be more active and vigorous than others. The members of the *halogen family* are the most active elements known. The word "halogen" means salt-producer. These elements form many of the important salts used in chemistry. In the majority of their compounds, these elements borrow electrons and have a negative valence of 1. As positive elements, they may have a valence as high as 7.

#### A. FLUORINE

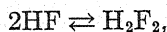
**335. Fluorine** is the most active element known. It combines readily with practically all elements but oxygen. It unites with hydrogen explosively, even in the dark. Nearly all elements are attacked by it, and the salts formed are called fluorides. Gold and platinum are attacked by it slowly. Fluorine is found in nature in *fluorite*, a mineral

composed of calcium fluoride,  $\text{CaF}_2$ . The only known method of preparing the element is the one worked out by Moissan. He decomposed *potassium acid fluoride*,  $\text{KHF}_2$ , by electrolysis.

**336. Hydrogen Fluoride,  $\text{H}_2\text{F}_2$ .** If we treat calcium fluoride,  $\text{CaF}_2$ , with sulfuric acid, hydrogen fluoride is set free.



Like hydrogen chloride, it is a colorless gas that fumes strongly in moist air. It dissolves in water and forms *hydrofluoric acid*. This acid is very corrosive, attacking the flesh and forming painful sores that require a long time to heal. The vapor is very dangerous when inhaled. Hydrofluoric acid attacks most substances; wax, lead, and platinum are the most important exceptions. At ordinary room temperature, the molecular weight of hydrogen fluoride is 40, showing that the gas has the formula  $\text{H}_2\text{F}_2$ . At somewhat higher temperatures, the molecular weight is only 20, corresponding to a formula of  $\text{HF}$ . The equation,



shows how two molecules *associate* at lower temperature to form a single molecule.

Hence, hydrofluoric acid may act as a dibasic acid.

The chief use for hydrofluoric acid is for etching glass.

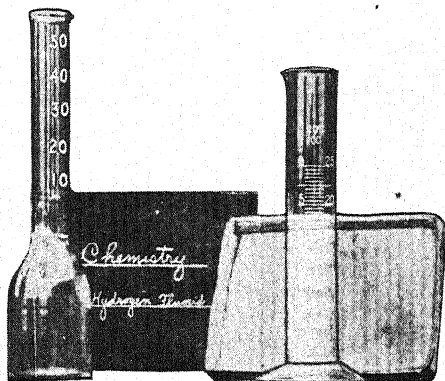


FIG. 207.—The word "chemistry" was etched with the gas hydrogen fluoride; the other words with a solution of the gas.

After the surface of the glass has been covered with wax or paraffin, a sharp stylus is used to scratch away the wax from the parts to be etched. Then the prepared glass plate is exposed either to the gas, or to a solution of hydrofluoric acid. (See Fig. 207.) The excess acid is washed off, and the paraffin is then removed. If a *solution* is used, the etching is smooth and transparent; if the *gas* is used for etching, the glass is likely to be rough and translucent. Fluorides are sometimes used for "frosting glass," in the making of enamels, and in the manufacture of certain kinds of glass.

### B. CHLORINE

**337. Where Chlorine Is Found.** Since chlorine is such an active element, it never occurs free or uncombined in nature. It occurs abundantly in chlorides. Sodium chloride, or salt, is widely distributed, occurring in salt brines underground, in sea water, and in rock-salt deposits. Sodium chloride is the commercial source of chlorine. Other chlorides found in nature are those of potassium and magnesium. It was first isolated by Scheele, a Swedish chemist.

**338. How Chlorine Is Prepared.** 1. *By electrolysis of sodium chloride.* Several commercial methods of preparing

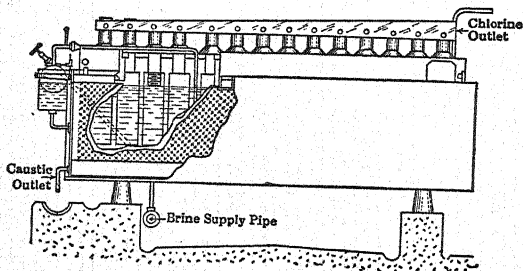


Fig. 208. — Sectional diagram of the Nelson cell.

chlorine by the electrolysis of a solution of sodium chloride have been developed. In all cases the sodium that is set

free at the cathode attacks the water and forms sodium hydroxide, which is a valuable by-product. But hydrogen is liberated at the same time, and the apparatus must be so devised that the hydrogen will not mix with the chlorine that is being liberated at the anode. A diaphragm is generally used for this purpose.

In the Nelson cell, Fig. 208, a narrow steel tank contains the electrolyte. A perforated, U-shaped piece of sheet iron serves as the cathode. Graphite rods, which are immersed in the salt solution, serve as the anodes. A closely woven asbestos diaphragm, supported by the sheet iron cathode, is used to keep the chlorine from uniting with the hydrogen or the sodium hydroxide. (See Fig. 209.)

After the United States entered the World War in 1917, the largest chlorine plant ever built was erected at Edgewood Arsenal, Maryland. In no other case had so extensive a chemical plant been built for electrolytic work. Figure 210 shows one of the eight cell rooms. One

hundred tons of chlorine could be produced daily in this plant.

2. *By the oxidation of hydrogen chloride.* (A laboratory method.) Manganese dioxide is an oxidizing agent. If it is mixed with hydrochloric acid, chlorine is set free when the mixture is heated. The equation follows:

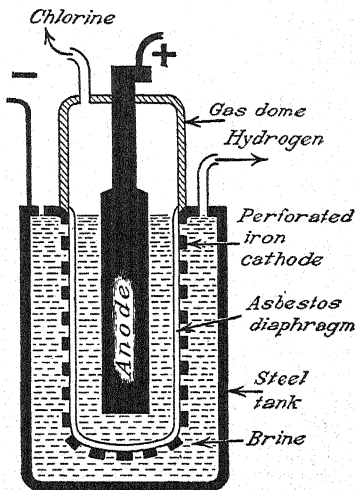
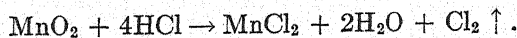


FIG. 209. — Cross-sectional diagram of Nelson cell.

There is an interesting valence change in this case, as in all oxidation and reduction reactions. The valence of the manganese in the dioxide is 4; but as the hydrogen of the hydrochloric acid is oxidized to form water, the valence of the manganese is lowered to 2. We would expect to have formed

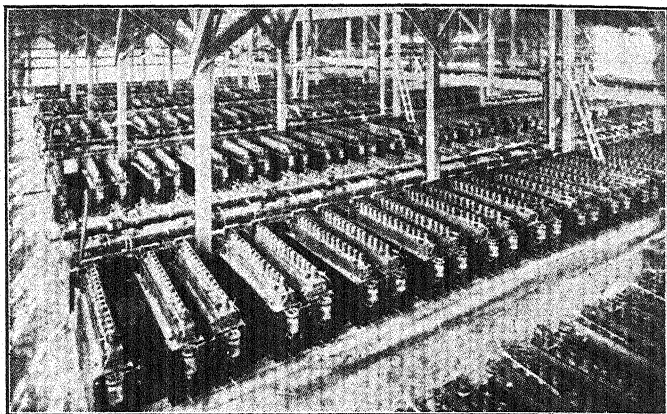


FIG. 210. — One of the eight cell rooms of the Edgewood Arsenal.

manganese tetra-chloride,  $\text{MnCl}_4$ , but if such a compound is formed at all, it decomposes immediately.

It is good laboratory practice to oxidize the hydrochloric acid as fast as it is formed. Hence manganese dioxide is mixed with sodium chloride and sulfuric acid. When this mixture is heated, the manganese dioxide oxidizes the hydrogen chloride, and chlorine is set free. The reaction takes place as represented by the following equation:



**339. Physical Properties.** Chlorine is a greenish-yellow gas, having a disagreeable, suffocating odor. It is about  $2\frac{1}{2}$  times as heavy as air, and moderately soluble in water. It imparts to the water solution a pale yellow color. When

inhaled in small quantities, it attacks the mucous membrane of the nose and throat, and produces the same effect as a heavy cold. The bad effects produced from breathing chlorine are partly alleviated by inhaling alcohol or ammonia. In larger quantities, chlorine is so toxic that it causes death.

**340. Chemical Behavior of Chlorine.** In the business world, chlorine would be called a "go-getter." Its activity is due to its greed for electrons. Fluorine is the only element that is more active. Under certain subtopics, we may list some of the activities of chlorine:

1. *Action with metals.* Let us sprinkle some powdered antimony into a jar of moist chlorine. The two elements unite spontaneously, emitting a shower of sparks. Antimony tri-chloride,  $\text{SbCl}_3$ , is formed. When we heat some metallic sodium and lower it into a jar of chlorine, sodium chloride is produced. Chlorine combines directly with such metals as copper, zinc, iron, and arsenic, if they are heated slightly.

2. *Action with hydrogen.* No action occurs if a mixture of hydrogen and chlorine is kept in the dark. But if heated, or exposed to sunlight, such a mixture explodes violently. A jet of hydrogen, burning in air, will continue to burn when introduced into a jar of chlorine. Hence our definition of combustion must be broadened to include *any chemical change that takes place so vigorously that both light and noticeable heat are produced*. Chlorine has so great an affinity for hydrogen that it can take hydrogen from some of its compounds. For example, although chlorine does not support the combustion of wood, paper, etc., yet a candle will continue to burn in it. The flame is smoky, and examination of the products left shows us that the hydrogen from the candle wax has combined with the chlorine, and that carbon is left uncombined. Turpentine is a hydrocarbon having the formula  $\text{C}_{10}\text{H}_{16}$ . If a strip of filter paper is moistened with warm turpentine and suspended in a jar of chlorine, it bursts into flame. Hydrogen chloride is formed, and dense clouds



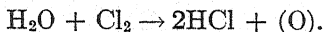
of soot are produced. Thus we see that *chlorine not only combines directly with hydrogen, but it has the ability to take hydrogen from hydrocarbon compounds.*

3. *Its action with water.* Freshly prepared chlorine water is yellow in color. If we let such a solution stand in sunlight for a few days, the yellow color, and the pronounced odor of



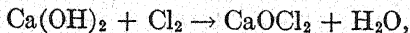
FIG. 211. — Bleaching effect of chlorine.

chlorine both disappear. The chlorine has united with the hydrogen of some of the water to form hydrochloric acid. The equation follows:



The water solution of chlorine is a vigorous *bleaching agent*. Since a substance must be wet to be bleached by chlorine, it seems evident that the bleaching action is one of oxidation due to the action between water and chlorine with the liberation of nascent oxygen. (See Fig. 211.) *Chlorine water* is a good oxidizing agent.

**341. Uses of Chlorine.** 1. *For bleaching.* For use in bleaching, chlorine may be obtained from *chloride of lime*, or *bleaching powder*. This compound, which is made by passing chlorine gas into calcium hydroxide,



is probably not a single compound, but a mixture of the salts of *hydrochloric* and *hypochlorous* acids corresponding to the formula  $\text{CaOCl}_2$ . Sometimes the article to be bleached is attached to the anode of a cell in which the electrolysis of sodium chloride is taking place.

Figure 212 shows a method used in bleaching cotton goods. The cloth is boiled in a dilute caustic soda solution to remove the wax from the fibers. From the roll, R, the cloth is drawn through a vat, b, containing bleaching powder and water.

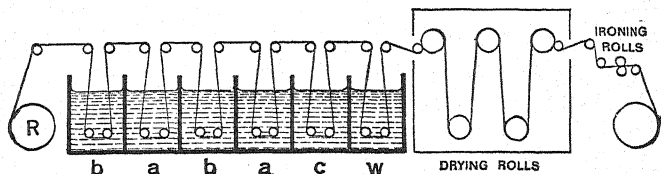


FIG. 212. — Commercial method of bleaching cotton goods.

Then it goes into a sulfuric acid vat, a, where hypochlorous acid is set free. An *antichlor* is used in vat c to remove the last traces of chlorine. The strip is then washed, ironed and re-rolled.

For removing stains or spots on cotton or linen, Labarraque's solution is often used. It is made by mixing a solution of sodium carbonate with a solution of calcium hypochlorite obtained by boiling water that contains bleaching powder. Such a solution is often *incorrectly* called *Javelle water*, which is a similar stain remover that contains potassium hypochlorite instead of sodium hypochlorite. Ink eradicators also use chlorine as the bleaching agent. Solution No. 1 contains citric or tartaric acid. Solution No. 2 contains some hypochlorite solution. When the two solutions are mixed, hypochlorous acid,  $\text{HClO}$ , is set free. Students must not get the idea that chlorine will bleach all dyes or destroy all colors. Many dye-stuffs are not affected by chlorine as a bleaching agent. Chlorine usually removes natural colors and takes

out spots made by ordinary ink, but it does not affect printer's ink at all. Chlorine finds extensive use in bleaching cotton goods. It must not be used with silk or wool. *Neither Labarraque's solution nor Javelle water can be used to remove spots or stains from silk or wool.*

2. *As a disinfectant.* Since moist chlorine is a good oxidizing agent, bacteria are destroyed by it. Large quantities of "chloride of lime" are used as a disinfectant. Billions of gallons of water are treated with chlorine to make it fit for drinking purposes. The water in the swimming pools in amusement parks, recreation buildings, or in parks is treated with chlorine to destroy disease-producing bacteria. Dakin's solution, so extensively used for sterilizing wounds, contains sodium hypochlorite. Chlorine is easily liquefied, and it is usually marketed in steel cylinders.

3. *For making compounds.* Chloroform contains a large percentage of chlorine. Carbon tetrachloride,  $\text{CCl}_4$ , is extensively used as a fire extinguisher. It is as efficient as gasoline for removing spots on clothing, and it has the advantage of being non-flammable. It costs slightly more than gasoline, but it is cheaper than a fire might be. Chlorine was made on a large scale during the World War because all the toxic gases were compounds of chlorine.

4. *As a toxic gas.* April 22, 1915, the Germans released great clouds of chlorine from rows of cylinders which had been secreted in their trenches. This heavy gas was carried by the winds to the Canadians at Ypres. The men were without masks, and the casualties were heavy. Within a week, the women in France and England made over 2,000,000 small bags and filled them with "hypo" crystals. This chemical is an "*antichlor.*" Even such a crude mask, when tied over the mouth and nose of a soldier, made him temporarily immune to the attacks of chlorine. More efficient masks were developed later by the chemists engaged in defensive work. They were capable of nullifying the effects of such

gases as mustard gas, chlor-picrin, and phosgene, all chlorine compounds that were used as poisonous gases during the World War. (See Fig. 213.)

★ 342. Phosgene,  $\text{COCl}_2$ . This toxic gas is made by passing carbon monoxide and chlorine over charcoal as a catalyst. It is especially dangerous, since a person who inhales it does not suffer from it for a few hours. Then he may collapse suddenly. It is suffocating and attacks the membranes of

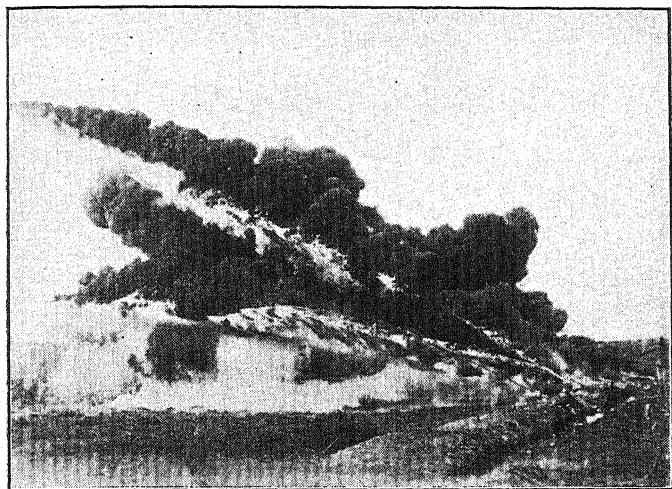


FIG. 213. — Photograph showing actual trench warfare.

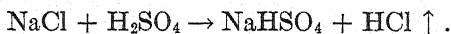
the respiratory organs; it tends to stop the action of the heart.

★ 343. Chlor-picrin,  $\text{CCl}_3\text{NO}_2$ . This compound is made by the interaction of bleaching powder and picric acid. It is a heavy liquid, which gives off a suffocating vapor that attacks the eyes, and also induces vomiting. The men who inhaled its vapor were thus forced to remove their masks. Other more deadly gases were used with chlor-picrin during the World War.

★ 344. **Mustard Gas,  $(C_2H_4Cl)_2S$ .** This compound, called "mustard gas," is known to chemists as *di-chlor-ethyl-sulfide*. It is an oily liquid that is made by absorbing ethylene,  $C_2H_4$ , in sulfur monochloride,  $S_2Cl_2$ . The liquid blisters the skin, and causes wounds that are slow to heal. As it *slowly* evaporates, a vapor is emitted that affects the lungs in a manner similar to pneumonia.

### C. HYDROGEN CHLORIDE

345. **How Hydrogen Chloride Is Prepared.** The commercial preparation of hydrogen chloride is the same as the method used for its laboratory preparation, heating sodium chloride with sulfuric acid.



The gas is dissolved in pure water, and marketed as *hydrochloric acid*. It is often called *muratic acid*.

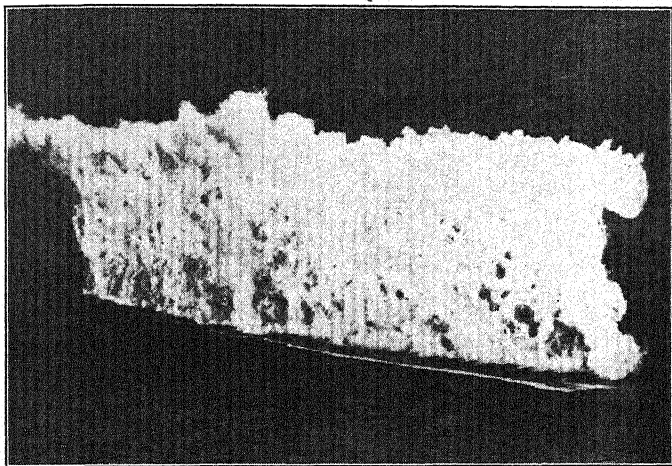
346. **Physical Properties.** Hydrogen chloride is a colorless gas that has a sharp, penetrating odor. It is heavier than air, and it dissolves readily in water. One volume of water at standard temperature and pressure will dissolve a little more than 500 volumes of the gas. Hydrogen chloride *fumes* in moist air, because it is so soluble that it takes water from the air and condenses it into minute drops.

347. **Chemical Behavior.** 1. *Stability.* Hydrogen chloride is a stable compound. It neither burns nor supports combustion, although some oxidizing agents attack it and liberate chlorine.

2. *As an acid.* A water solution of hydrogen chloride is known as hydrochloric acid. The *concentrated* acid contains about 38% of the gas by weight. It is nearly 1.2 times as dense as water. When the concentrated acid is boiled, it loses hydrogen chloride gas faster than it does water, and the solution becomes more dilute, until it contains only 20% of the gas by weight. If, however, we boil a more dilute

solution, it loses water faster than it does the gas, and the acid becomes more concentrated, until it is of 20% strength. A 20% solution boils at 120° C., and its strength remains constant. Hydrochloric acid is one of the strongest acids known. It attacks metals, oxides of metals, and neutralizes bases.

**348. Uses.** Hydrochloric acid is used in making chlorides, in preparing bleaching powder, and in cleaning metals.



*Courtesy U.S. War Dept.*

FIG. 214. — A curtain of chemical smoke laid down by an airplane.

Many metals must be freed from their oxides and other forms of tarnish before they can be galvanized, tinned, enameled, or plated with other metals. The process of removing such scale is known as "pickling." The metals are immersed in a mixture of acids, usually hydrochloric and sulfuric in varying proportions. Some hydrochloric acid is present in the gastric juice of the stomach. Probably many stomach disorders are due either to a deficiency of this acid in the gastric juice, or to the presence of too large a percentage.

**349. Chlorides.** There are chlorides of nearly all the metals. They form an important group of salts. In addition, the chlorides of such non-metals as carbon, phosphorus, sulfur, hydrogen, and silicon are well known compounds that have important applications. The chlorides of the metals are nearly all crystalline compounds; most of them

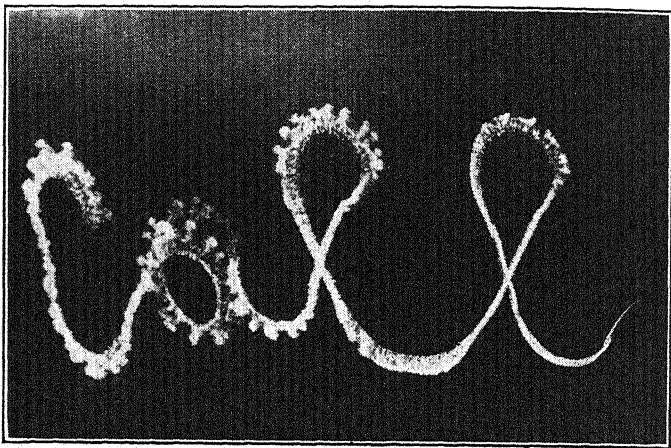


FIG. 215. — Writing upon the sky in letters one mile high.

are water-soluble. The *chlorides of silver, lead, and mercurous mercury* are insoluble.

★ **350. The Chemical Nature of Smoke Screens.** Such elements as tin, titanium, and silicon form tetra-chlorides that hydrolyze almost completely in moist air. As they hydrolyze, hydrogen chloride is formed, and it condenses the moisture in the air to form a mist. The tetra-chlorides of silicon and titanium were extensively used during the World War to make a smoke screen to hide the movements of vessels or of troops. When ammonia was used with them, it combined with the hydrogen chloride and formed particles of ammonium chloride. (See Fig. 214.)



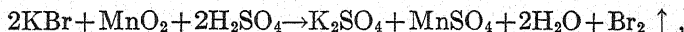
"Chemical smoke" is used in airplanes for making "screens" and also for advertising by "sky-writing." At a height of about 2 miles a pilot writes his message in letters of "smoke." The letters are from a half mile to a mile in height. From 6,000,000 to 8,000,000 cu. ft. of "smoke" are required for each letter. The "smoke" is released as the pilot travels from 75 to 120 miles per hour. (See Fig. 215.)

**351. Test for Chlorides.** To test for a soluble chloride, we make use of Berthollet's law of insolubility. To the solution to be tested for chloride ions, we add a solution of silver nitrate. If a chloride is present, its chloride ion will unite with the silver ion to form a white precipitate of silver chloride, which is insoluble in nitric acid. The test is not satisfactory in the presence of bromides or iodides.

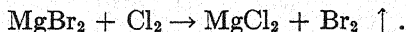
#### D. BROMINE

**352. How Bromine Is Found.** Several bromides are found in nature; the most abundant are the bromides of sodium and magnesium. The chief source of bromine is the "mother liquor" left after the sodium chloride has been extracted from the brine of salt wells. Bromides are found in the deposits of the salts of the alkali metals at Stassfurt, Germany. The United States and Germany are the only countries where any considerable quantities of bromine are found.

**353. How Bromine Is Prepared.** It is possible to prepare hydrogen bromide by the action of sulfuric acid on a bromide, and then oxidize the hydrogen bromide with manganese dioxide. The equation,



shows that the method of preparation is exactly analogous to that of preparing chlorine. Commercially, bromine is prepared either by electrolysis of a bromide, or by decomposing magnesium bromide with chlorine:





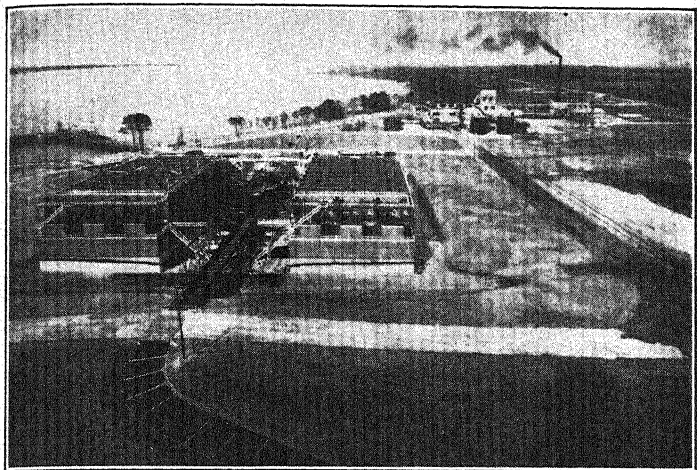
The salt wells of Ohio, Michigan, and West Virginia are the chief sources of supply in the United States.

**354. Physical Properties.** Bromine is a dark-red liquid about three times as dense as water. Bromine and mercury are the only elements that are liquid at the ordinary temperature. Bromine is quite volatile. Its vapor has a very disagreeable odor, and it irritates the eyes and throat. The name comes from the Greek word *bromos*, which means "stench." Great care must be used in handling bromine, for it burns the flesh frightfully. Few liquids are as corrosive. Bromine is moderately soluble in water, forming a reddish-brown solution which is used in the laboratory under the name *bromine water*.

**355. Chemical Behavior.** Bromine resembles chlorine in its chemical properties, but it is less energetic. With hydrogen, it unites slowly to form *hydrogen bromide*. It combines directly with many metals to form bromides. It is a bleaching agent when moist. Its water solution is a good oxidizing agent. In sunlight, such a water solution forms hydrobromic acid and liberates oxygen.

**356. Uses of Bromine.** In the manufacture of certain dye-stuffs, bromine finds some use. It was used during the World War for making tear gases. Bromine finds use in the manufacture of bromides.

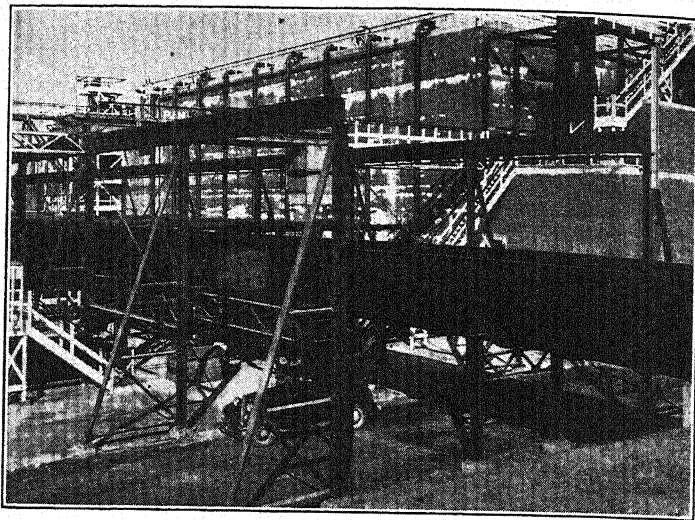
**357. The Bromides.** The *bromides of sodium and potassium* are used in medicine as a sedative to quiet the nerves. They should not be used except when prescribed by a physician. *Silver bromide* is a yellowish solid that finds extensive use as the sensitive salt for photographic plates. It is decomposed by light in the presence of a reducing agent. *Ethylene bromide*,  $C_2H_4Br_2$ , is used with tetra-ethyl lead in making "anti-knock" gasoline. This application has enormously increased the demand for bromine. Practically all the "tear gases" used during the World War to temporarily blind the enemy were either bromides or bromine com-



*Courtesy of Dow Chemical Co.*

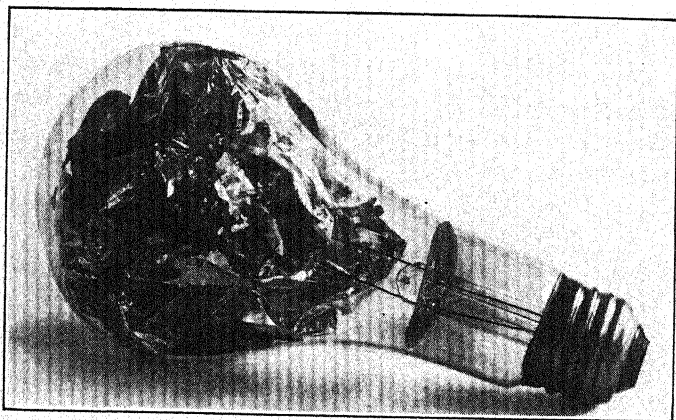
General view of plant for making bromine from sea water.

The sea contains enormous quantities of mineral matter, but it is in such small concentration that it is very difficult to extract such minerals at a profit. Chemists have dreamed of getting gold from sea water. If tetra-ethyl lead is used in gasoline, ethylene di-bromide must be used with it to make it more efficient. Hence the demand for bromine has increased some 450% within the last few years. After sampling the sea water along the Atlantic coast for bromine, the Dow Chemical Company built a plant for taking the 70 parts of bromine from 1,000,000 parts of water. The plant, which was built in 1933, is capable of extracting 15,000 pounds of bromine daily from the 58,000 gallons of sea water which are pumped per minute through the extraction plant.



*Courtesy of Dow Chemical Co.*

The sea water is carried through the half-round conduit in front to the extraction plant in the rear.

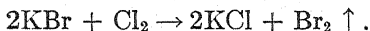


*Courtesy of Westinghouse Lamp Co.*

The flashlight bulb is filled with aluminum foil and oxygen. The large surface area permits almost instantaneous oxidation when the foil is ignited by the filament.

pounds. *Xylol bromide*, when present to the extent of only two or three parts per million of air, causes a copious flow of tears. *Brom-acetone* was also used as a lachrymator. Tear bombs are used by the police to quell riots or to drive barricaded criminals out into the open.

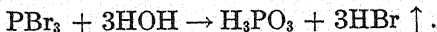
**358. How to Test for Bromides.** Bromine is very soluble in carbon disulfide, and it colors the liquid an orange-red. When chlorine water is added to a water solution of a bromide, the chlorine will displace the bromine. For example,



These facts are utilized in testing for bromides in solution. To the unknown solution chlorine water and about 1 c.c. of carbon disulfide are added. The mixture is thoroughly shaken. The chlorine displaces any bromine that may have been present as a bromide, and the bromine, being much more soluble in carbon disulfide than in water, dissolves largely in the carbon disulfide. The carbon disulfide does not mix with the water, but it settles to the bottom. If a bromide is present, the carbon disulfide will appear as an orange-red globule.

**359. Hydrogen Bromide.** Some hydrogen bromide, which is analogous to hydrogen chloride, is prepared when a bromide is treated with sulfuric acid. But it is more unstable than hydrogen chloride, and part of it is decomposed by the heat of the reaction. The hydrogen that is formed by such decomposition reduces some of the sulfuric acid; hence this method of preparing hydrogen bromide yields a product contaminated with sulfur dioxide and free bromine.

Phosphorus tri-bromide hydrolyzes in water solution as represented by the equation,



This method of preparing hydrogen bromide gives an uncontaminated product. The gas is dissolved in water to

form *hydrobromic acid*. The solution has all the properties of a strong acid.

### E. IODINE

**360. Where Iodine Is Found.** The element iodine was discovered by Courtois, a French chemist, who noticed the purplish vapor of iodine that he obtained while investigating the ashes from seaweeds. For some time nearly all the iodine of commerce was extracted from seaweeds that were washed ashore along the coasts of France, Scotland, and other European countries. The chief source of iodine at present is Chile, where it is found as sodium iodate,  $\text{NaIO}_3$ , in the nitrate deposits.

**361. How Iodine Is Prepared.** The method of preparing iodine is analogous to that for preparing chlorine and bromine. Some iodide is heated with manganese dioxide and sulfuric acid. The equation follows:



The iodine is driven off as a vapor, which may be condensed as a solid on the walls of a cold dish or beaker.

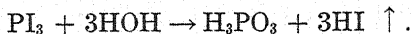
**362. Physical Properties.** Iodine is a steel-gray, crystalline solid. When heated, it *sublimes*, or vaporizes without melting. Its vapor is a beautiful violet color, but its odor is irritating and it resembles that of chlorine to some extent. Iodine is only *slightly* soluble in water. It dissolves readily in alcohol, forming the *tincture of iodine*. A solution of iodine in carbon disulfide has a beautiful purple color. While iodine is scarcely soluble in water, it will dissolve readily in a water solution of potassium iodide.

**363. Chemical Behavior of Iodine.** Iodine is active chemically, though less so than either chlorine or bromine. It combines with many metals to form iodides. It combines with some non-metals. If a crystal of iodine is placed on a piece of white phosphorus, they unite with the evolution of

light and heat. Either chlorine or bromine will displace iodine from solutions of iodides. Free iodine colors starch paste blue. This color change serves as a test for free iodine; or if we have given an iodine solution, it serves as a test for starch.

**364. Uses of Iodine.** Iodine is used in medicine, in photography, and for making dye-stuffs. The tincture of iodine contains 7% of iodine dissolved in alcohol, or in a solution of potassium iodide. It is used as a counter-irritant to reduce swellings. If a bottle of tincture of iodine is left unstoppered, the solvent will evaporate, and the tincture will become strong enough to blister the skin. Such blistering may result from covering the part that has been painted with the tincture, or from a second application. Iodine is poisonous if taken internally. Starch paste or starchy foods may be used as an antidote. Iodine is used as an antiseptic for sterilizing wounds or to paint the skin before an incision is made during an operation.

**365. Hydrogen Iodide and Metallic Iodides.** Very little hydrogen iodide is obtained when we try to prepare it by treating an iodide with sulfuric acid. Hydrogen iodide is less stable even than hydrogen bromide. It decomposes and reduces the sulfuric acid; thus any hydrogen iodide that does not decompose is contaminated with iodine, and with hydrogen sulfide as a reduction product from the sulfuric acid. The pure gas is prepared by the hydrolysis of phosphorus tri-iodide:



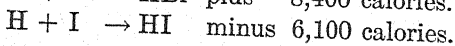
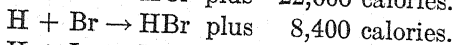
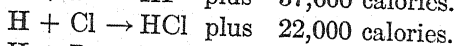
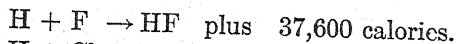
Hydrogen iodide is a colorless gas, which dissolves in water and forms *hydriodic acid*. The solution is a strong acid.

Several iodides are useful. *Silver iodide*, AgI, finds use in photography. *Potassium iodide*, KI, finds use in medicine. Iodine is present in the thyroid gland of the body. Some physicians believe that the iodine regulates the growth of this gland and prevents the formation of goiter. Hence iodine

is added to the water in certain localities where goiter is common. The iodine is used in the form of sodium or potassium iodide. Some companies are adding this compound to table salt to make "iodized" salt.

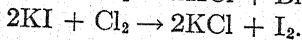
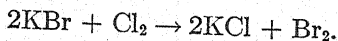
#### F. RELATIVE STABILITIES OF HALOGEN COMPOUNDS

**366. Relative Stabilities.** We learned that hydrogen and fluorine will combine with hydrogen *in the dark*; chlorine combines with hydrogen explosively *in sunlight*; bromine unites with hydrogen *more slowly*; it requires heat energy to make hydrogen combine with iodine. The amount of heat liberated or absorbed during the formation of one mole of each of the halogen compounds is shown in the following equations:

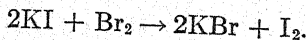


The ease with which these compounds can be decomposed is in the reverse order to the ease with which the elements unite to form the compounds.

The relative stability of the halogen compounds can also be determined by the ability of one halogen to displace another. Fluorine can displace any one of the other three halogens. Chlorine can displace either bromine or iodine. See equations:



Bromine can displace iodine from its compound, but it cannot displace either fluorine or chlorine. The equation follows:



These reactions are exactly what one would expect from the thermal equations shown above. We learned that the



displacement of bromine by chlorine can be used as a test for a soluble bromide, because the bromine colors carbon disulfide an orange-red. In a similar manner one can test for the presence of an iodide in solution by adding chlorine water to the solution and shaking the mixture with several drops of carbon disulfide. The iodine which is set free by the chlorine colors the carbon disulfide a violet or purple.

## SUMMARY

*Fluorine, chlorine, bromine, and iodine* comprise the halogen group. They form some of the important salts used in chemistry.

Fluorine is isolated by the electrolysis of potassium acid fluoride. The other three halogens are prepared by oxidizing their hydrogen acids with manganese dioxide.

The acids of the halogens may be prepared by treating a salt of the acid with sulfuric acid. Hydrogen bromide and hydrogen iodide are prepared by the hydrolysis of phosphorus tri-bromide and phosphorus tri-iodide.

*Fluorine* compounds are used for etching glass. *Chlorine* is used for bleaching, disinfecting, making chlorides, and for making poison gases and smoke screens. *Bromine* is used in the dye industry, for making medicines, in photography, and for making tear gases. *Iodine* is used medicinally.

The following table shows comparatively the properties of the halogens:

Properties	Fluorine	Chlorine	Bromine	Iodine
Atomic weight.....	19	35.5	80	127
State.....	gas	gas	liquid	solid
Principal valence.....	1	1	1	1
Boiling point.....	- 187° C.	- 34° C.	59° C.	184° C.
Activity.....	most	less	still less	least
Formula of hydrogen acid	HF	HCl	HBr	HI
Stability of hydrogen acid	most	less	still less	least
Heat of formation of hydrogen acid.....	37,600	22,000	8,400	- 6,100
Replacement.....	replaces Cl, Br, and I	replaces Br and I	replaces iodine	



## QUESTIONS

## GROUP A

1. Compare the chemical action of chlorine, sulfur dioxide, ozone, and hydrogen peroxide as bleaching agents.
2. Balance and complete the following equations:  
(a)  $\text{Cu} + \text{Cl} \rightarrow$       (b)  $\text{As} + \text{Cl} \rightarrow$       (c)  $\text{Zn} + \text{Cl} \rightarrow$
3. Why should chlorine water be kept in dark-colored bottles?
4. Hydrofluoric acid is put on the market in wax bottles, or in wax-lined containers. Explain.
5. How would you test for the presence of a fluoride? Of a chloride? Of a bromide? Of an iodide?
6. How would you test for free iodine? For combined iodine?
7. What precautions must one use with hydrofluoric acid?
8. Why is it impossible to remove printer's ink stains with chlorine?
9. What is meant by sublimation? How can it be used to purify iodine?
10. Why are the halogens not found free in nature?
11. Write equations for four methods of preparing copper chloride.
12. Sea-foods, especially oysters, lobsters, etc., are rich in iodine. Why are they especially desirable for food?
13. Is it possible to have combustion without oxygen? If so, give an example, and tell what product is formed.
14. Is it possible to produce a fountain with hydrogen chloride similar to the one described under ammonia?

## GROUP B

15. Give two reasons why nitric acid is not suitable for use in preparing hydrogen chloride.
16. Why do solutions of hydrogen iodide become dark-colored?
17. From the source of bromine, what do you infer concerning the relative solubilities of chlorides and bromides?
18. Why do we not get metallic sodium when a solution of sodium chloride is electrolyzed?
19. How would you proceed to frost the inside of an electric bulb? How would you mark the degrees on a thermometer?

20. A metal plate is attached to the negative terminal of a battery. Upon the plate is a dilute starch paste to which some potassium iodide has been added. If one end of a wire is attached to the positive terminal of the battery, a blue mark appears when the other end is drawn through the paste. Explain.

21. After chlorine has been used to bleach cotton, an antichlor must be used to destroy the chlorine left in the fiber. Why?

22. Is it possible for hydrofluoric acid to form acid salts? Can any other of the halogen acids form acid salts? Explain.

23. Write the equation for the burning of turpentine in chlorine. What products are formed?

24. How would you expect a freshly prepared solution of chlorine in water to react toward litmus? How would the same solution react after standing in sunlight for a few days?

## PROBLEMS

### GROUP A

1. What weight of bromine can be obtained from 250 gm. of magnesium bromide?

2. How many tons of sodium hydroxide are formed while making 60 tons of chlorine by the electrolysis of chloride?

### GROUP B

3. How many liters of chlorine at S. T. P. can be prepared from 200 gm. of sodium chloride?

4. How many liters of hydrogen fluoride can be obtained by the action of an excess of sulfuric acid on 390 gm. of calcium fluoride at 20° Centigrade and 750 mm. pressure?

## SUPPLEMENTARY PROJECTS

Prepare a report on one of the following topics:

1. The work of Moissan in preparing fluorine.

Reference: *Encyclopedia Britannica*.

2. The work of Scheele.

Reference: *Encyclopedia Britannica*.

3. Poison gases in the World War.

Reference: LEFEBURE, V., *Riddle of the Rhine*. The Chemical Foundation, Inc.

## CHAPTER 26

### PERIODIC LAW — ATOMIC NUMBERS

#### Vocabulary

**Amphoteric.** Referring to a compound which may ionize as a base in the presence of a strong acid, and as an acid in the presence of a strong base.

**Isotopes.** Different forms of the same element, differing only in their atomic weights.

#### A. PERIODIC LAW

**367. How Elements Are Classified.** If the student were to study each element as an individual, his task would be difficult. Hence several attempts to classify elements have been made. We have just studied the halogens as a group or family of elements. They are so similar in their chemical properties that a knowledge of one of them enables one to predict with considerable accuracy the chemical behavior of the others. Several other elements may be grouped in a similar manner into *families*.

The earliest attempts to group elements classified them as *metals* and *non-metals*, or *base-formers* and *acid-formers*. But such a classification does not help enough in the study of chemistry. Some elements are acid-formers under some circumstances, and base-formers when the conditions are different. The hydroxides of those elements that ionize as an acid under some conditions and as a base under other conditions are said to be *amphoteric*. Various attempts have been made to find some relationship between chemical properties and atomic weights.

**368. Early Attempts at Classification.** As early as 1817, Dobereiner noticed that the atomic weight of bromine is an arithmetical mean between the atomic weights of chlorine

and iodine.  $(127 + 35.5) \div 2 = 81.25$ . The same holds true for calcium, strontium, and barium.  $(40 + 137) \div 2 = 88.5$ . The atomic weight of strontium is a little less than 88. The atomic weight of selenium is practically an arithmetical mean between the atomic weights of sulfur and tellurium.  $(32 + 127.5) \div 2 = 79.75$ .

The atomic weight of selenium is 79.2. Such groups of elements are known as *triads*.

In 1864 Newlands grouped all the elements in the order of their atomic weights. He then divided the elements into groups of seven elements each. He made such a division, because the eighth element was found to have properties similar to the first element of the preceding group. But he could not interest the chemists of his day in his *law of octaves*. Finally, the ridicule with which he met became so great that he stopped his work along the line of classification.

Lothar Meyer in Germany and Mendelejeff in Russia each worked out a complete system for grouping elements according to their atomic weights. In their systems the first two periods have *seven elements* each. Then there are three long periods of *seventeen elements* each. (See Fig. 216.)

**369. Mendelejeff's Periodic Law.** In this country the work of Mendelejeff, in his attempts to classify elements, is

69 Tl 204.4	68 Pb 207.2	67 Bi 208.0	66 Po 209.0	65 At 210.0	64 Rn 222.0
59 K 39.1	58 Ca 40.1	57 Sc 44.9	56 Ti 47.9	55 V 50.9	54 Cr 52.0
49 Rb 85.4	48 Sr 87.6	47 Y 88.9	46 Zr 91.2	45 Nb 92.9	44 Mo 95.9
39 Na 23.0	38 Mg 24.3	37 Al 26.9	36 Si 28.1	35 P 30.9	34 S 32.1
29 Cu 63.5	28 Ni 58.7	27 Co 58.9	26 Fe 55.8	25 Mn 54.9	24 Cr 52.0
19 F 19.0	18 O 16.0	17 N 14.0	16 C 12.0	15 B 10.8	14 Be 9.0
9 Li 7.0	8 He 4.0	7 H 1.0	6 C 12.0	5 B 10.8	4 Be 9.0

(Courtesy of P.)

generally considered the most successful. He believed that the chemical properties of elements are functions of their atomic weights.

Omitting hydrogen, suppose we arrange the elements in the order of their atomic weights, and examine the first eight.

	Vocal	C	N	O	F
Amphoteric. Referring to a cor		12	14	16	19

in the presence of a strong acid  
a strong base.

Isotopes. Different forms of the  
their atomic weights.

lithium is metallic, a very  
(sometimes called glucinum,  
ber; boron may form a base,

A. PERIODIC a weak acid; carbon forms a  
strong acids; oxygen is charac-

**367. How Elements Are Classified.** It is the most active non-metal  
to study each element as an individual. Hence several attempts have been made. We have just studied the tendency to form strong  
or family of elements. They are listed below the first eight.  
properties that a knowledge of the first eight elements,  
predict with considerable accuracy the tendency to form strong

	C	N	O	F
of the others. Several other	12	14	16	19

	Si	P	S	Cl
similar manner into families.	28	31	32	35.5

The earliest attempts to group elements were made by Berzelius, who divided them into *metals* and *non-metals*, or *base-forming* and *acid-forming*.  
such a classification does not hold in all  
chemistry. Some elements are amphoteric; sodium is also a strong  
circumstances, and base-forming; magnesium is similar to  
beryllium, Thallium, Indium, and Boron; like carbon, silicon is a  
weak acid-forming element; phosphorus resembles nitrogen  
in its chemical properties; sulfur is like oxygen chemically;  
and chlorine is very active like fluorine.

By arranging all the elements in the order of their atomic weights, Mendelejeff discovered that the properties of the elements recur at regular intervals. He therefore concluded that the properties of elements are periodic functions of their



like calcium in its chemical behavior. The atomic number of each element is given in this table.

**371. Value of the Periodic Law.** 1. *It simplifies chemistry.* We have already seen that the grouping of elements into families makes the study of the properties and behavior of elements less difficult to grasp and retain.

2. *It serves as a check on atomic-weight determinations.* When the periodic table was first prepared several of the elements were not properly placed. The suggestion that this might be due to errors in the atomic-weight determinations seemed plausible. More accurate methods were used, giving new values for certain atomic weights. Upon the substitution of these new values, many elements then fitted into their proper places in the table.

3. *In the prediction of new elements.* There were several gaps in the table, which led Mendeleeff to predict the existence of undiscovered elements, having properties and atomic weights that make them fit into these gaps. In fact, within a few years immediately following the announcement of Mendeleeff's law several elements were discovered whose properties and atomic weights are very nearly in accord with what he had predicted. The remarkable agreement between the predicted properties of *eka-aluminum* and the actual properties of *gallium* are shown in the following table:

	Predicted	Discovered
Atomic weight.....	About 69	69.7
Melting point.....	Low	30.2°
Specific weight.....	5.9	5.95
Formula of oxide.....	X <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>
Action of air.....	None	Slight, even at red heat

Since this element was discovered in France, it was named gallium. Mendeleeff also predicted the properties of *eka-boron*

(scandium) and *eka-silicon* (germanium) with practically equal accuracy. Other elements, more recently discovered, have found places in the table. The table now seems complete, but there is no place in it for the rare earths.

**372. The Periodic Law Is Not Perfect.** A careful examination of the periodic table shows several discrepancies. (1) There is no place for hydrogen in the table. (2) There were several blank spaces in the table, but these have been gradually filled as new elements have been discovered. (3) If the elements are arranged in the order of their atomic weights, the positions of potassium and argon must be changed. But it would be ridiculous to put potassium in a group with the rare, inactive gases, or to place argon with the active metals of Group 1. Iodine and tellurium are two other elements whose order must be changed to make them fit into the table properly. (4) The valence indicated by the use of the table is not the only valence, and it is not always the most common valence. For example, copper, shown in Group 1, more often has a valence of 2 than it has of 1. A table based on atomic numbers is more accurate.

## B. ATOMIC NUMBERS

**373. How Atomic Numbers Are Determined.** In Section 135 we learned that Moseley was able to determine the atomic numbers of the elements. The X-rays are ether waves that have a high frequency and a short wave length. Moseley discovered that the length of these X-ray waves depends upon the kind of metal that is used as a target, or anti-cathode. He therefore used various metals from aluminum to gold as targets for the cathode rays, and found that the X-ray waves become shorter as the number of excess protons in the nucleus of the element increases. Hence the atomic number increases as the length of the waves of the X-rays, when affected by the properties of the element used as a target, decreases. (See Fig. 217.) Moseley found that be-



tween certain successive pairs of elements the variation in the length of the X-ray waves was twice as great. He concluded that in such cases an element was missing from the table; several have since been discovered to fill the gaps indicated by such double variation in the wave length. Moseley numbered the elements from 1 to 92 as shown on page 433. By use of such a method, Hopkins discovered the element *il-linium*.

**374. New Periodic Law.** When the elements are arranged in the order of their atomic numbers, the discrepancies

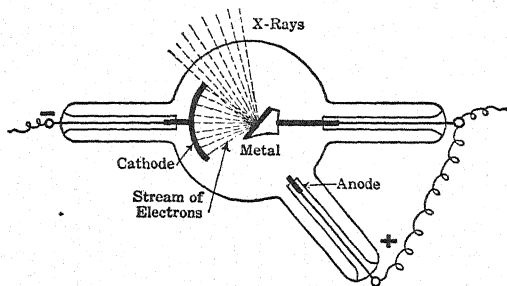


FIG. 217. — X-ray tube.

noted in the periodic table disappear. The atomic number of argon is 18, and that of potassium is 19. In the light of atomic numbers, the periodic law may be modified as follows: *The chemical properties of elements are periodic functions of their atomic numbers.* In other words, *the chemical properties of elements recur after certain intervals, when the elements are arranged in the order of their atomic numbers.*

### C. ISOTOPES

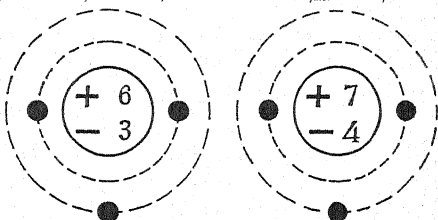
★ **375. What Are Isotopes?** From what we have learned concerning the structure of atoms, we would expect that the atomic weights of all atoms would be whole numbers. They are all made up of protons and electrons. The proton has

essentially the same weight as the hydrogen atom, and the weight of the electron is so small that it is practically negligible. A few years ago J. J. Thomson and T. W. Aston showed that some elements are really mixtures of atoms that have the same properties, but different whole number atomic weights. Chlorine, for example, whose atomic weight is given as 35.46, is a mixture of chlorine atoms that have an atomic weight of 35 with other chlorine atoms that have an atomic weight of 37. *Different forms of the same element, which differ only in the weights of their atoms, are known as isotopes.* The atomic weight of an element is therefore the average of the atomic weights of its isotopes.

The properties of the different isotopes are the same, because there are always the same number of planetary electrons. The difference in the weights is due entirely to the difference in their nuclei. Figure 218 shows two isotopes of lithium, in which the nuclei have 6 and 7 protons, respectively. But there are 3 electrons in the nucleus in one case, and 4 in the other. Hence, the number of excess protons in the nuclei of both isotopes is exactly the same, and the atomic numbers are the same. Several elements are known that have several isotopes.

Lithium, At. Wt., 6

Lithium, At. Wt., 7



## SUMMARY

Elements are grouped as *metals* and *non-metals*; they are also classed as *acid-forming* elements and *base-forming* elements.

Mendelejeff arranged the elements in the order of their atomic

weights. He then formulated the law that the *properties of elements are periodic functions of their atomic weights*.

The periodic law is of value: (1) in classifying elements and thus simplifying the study of chemistry; (2) it serves as a check upon the accuracy of atomic-weight determinations; (3) it indicated the presence of undiscovered elements in the earth's crust and on several occasions accurate predictions were made concerning the properties and atomic weights of elements even before their discovery.

Moseley found that he could use the X-ray to determine the atomic number of an element. An increase in the number of excess protons in the nucleus of a metal, used as the target in an X-ray tube, decreases the wave length of the X-rays it produces. The chemical behavior of an element seems to bear a definite relation to its atomic number.

Different forms of the same element, which differ only in their atomic weights, are called *isotopes*. Some elements are made up of two or more isotopes. The atomic number used by chemists is the average of the atomic weights of its isotopes.

## QUESTIONS

### GROUP A

1. Write the formulas for the oxide, hydroxide, sulfate, and carbonate of strontium.
2. Aluminum hydroxide is insoluble in water. What do you infer concerning the solubility of the hydroxide of scandium?
3. What properties would you expect caesium to have?
4. How can the periodic table be used in the study of chemistry?
5. From the periodic table, pick out several elements that you would expect to form strong bases.
6. From the periodic table, pick out several elements that should be strong acid-formers.

### GROUP B

7. It has been reported that a chemist succeeded in building up an element whose atomic number is 93. If true, what properties would you expect the element to have?

8. Look over the list of atomic weights and name several elements that you would expect to be isotopes.

9. Why is the periodic table based on atomic numbers more valuable than a table based on atomic weights?

## SUPPLEMENTARY PROJECT

Prepare a report on the following topic:

1. Kendall's "apartment house" conception of the grouping of elements.

Reference: KENDALL, JAMES, *At Home Among the Atoms*.  
D. Appleton-Century Co.



## CHAPTER 27

# THE NITROGEN FAMILY

### Vocabulary

**Alloy.** A solid solution of one or more metals in another metal.

**Mordant.** A chemical used to fix the dye in a fabric and make it fast.

**Fusible.** Easily melted.

**Taxidermist.** One who prepares mounted specimens of birds or animals.

**Photo-micrograph.** A photograph taken with a camera that has a microscopic attachment.

**Non-friction.** Referring to alloys that have little friction, or offer little resistance to the sliding of a metal over them.

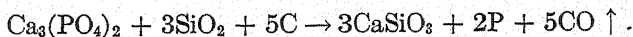
**Translucent.** Letting light shine through, but not clear enough to enable objects to be seen through it.

**376. The Nitrogen Family.** In Chapter 25 we studied the halogens as a family of elements. From the periodic table, we learn that there are several groups of elements whose members have family resemblances. *Nitrogen* is the most important element in the nitrogen family. If the student keeps in mind the chemical behavior of nitrogen, which we have already studied, he will have less trouble during the study of the other elements of this family, viz.: *phosphorus*, *arsenic*, *antimony*, and *bismuth*. Nitric acid is a strong acid, but the acid-forming properties of the elements of this family decrease as the atomic weights increase, or from nitrogen to bismuth. Nitrogen forms one of the strongest acids known. Phosphoric acid is much weaker; antimony and bismuth may act as base-formers. The valence of this family of elements is either 3 or 5, although nitrogen may also be 1, 2, or 4.

## A. PHOSPHORUS

**377. Where Phosphorus Is Found.** Phosphorus is too active an element to be found free in nature. The most important compound that contains this element is *rock phosphate*, or *calcium phosphate*,  $\text{Ca}_3(\text{PO}_4)_2$ . The bones and teeth of vertebrate animals contain calcium phosphate. Extensive areas of rock phosphate are found in Florida, Tennessee, and South Carolina. These beds furnish the phosphate needed for fertilizing soils that are deficient in phosphates. All plants must have phosphorus for their development. It is also present in our nerve, brain, and muscle tissues. Enormous deposits of rock phosphate have been discovered in the Northern Rockies near Yellowstone Park, but the industry is still undeveloped in that area. Rock phosphate deposits are probably accumulations from the bones of pre-historic animals.

★ **378. How Phosphorus Is Prepared.** In 1669 Brand discovered phosphorus while he was distilling urine in an attempt to find "the philosopher's stone." It was isolated by Scheele in 1771. Today it is made by heating calcium phosphate with a mixture of sand and coke in an electric furnace. Into a furnace of the type shown in Fig. 219, the mixture is fed by a worm conveyor. The resistance between the two electrodes near the bottom of the furnace is so great that much of the electrical energy is transformed into heat energy. At the high temperature produced, a reaction represented by the following equation occurs:



The calcium silicate forms a slag which is drawn off from the bottom of the furnace. The phosphorus and carbon monoxide pass out of the furnace, and the phosphorus is cooled by water and cast into sticks.

**379. Properties.** Phosphorus exists in two important

allotropic forms: *white* or *yellow* phosphorus, and *red* phosphorus.

1. *White phosphorus*. When freshly prepared, phosphorus is nearly colorless, or a pale straw color. Since it is usually a pale lemon color it is often known as yellow phosphorus. White phosphorus is a waxy, translucent solid,

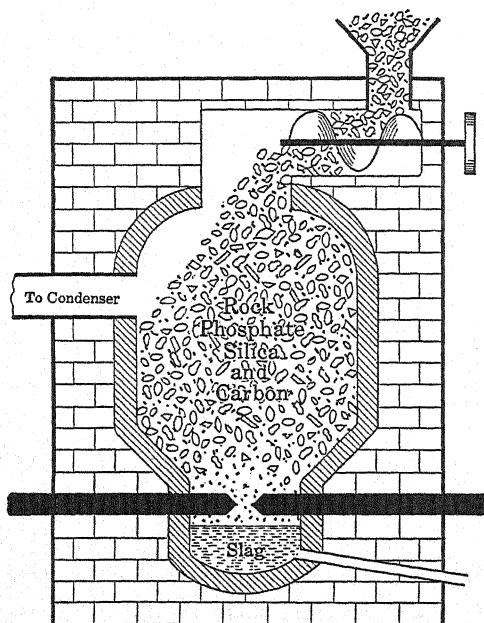


FIG. 219. — Electric furnace for making phosphorus.

nearly twice as dense as water. It melts at  $44^{\circ}\text{C}.$ , but since its kindling temperature is only  $35^{\circ}\text{C}.$ , it must be melted under water to prevent combustion.

*White phosphorus must never be handled with the fingers, since burning phosphorus produces poisoned wounds that require a long time to heal. It is very poisonous if taken internally, a small fraction of a gram being a fatal dose. White*

phosphorus is soft enough to be easily cut with a knife, but *it must always be cut under water* to prevent the heat from the friction of the knife from kindling it. Phosphorus is insoluble in water, but white phosphorus dissolves readily in carbon disulfide and in oils.

Phosphorus oxidizes readily when exposed to the air, giving off dense white fumes of phosphorus pentoxide,  $P_2O_5$ . If this oxidation occurs in a dark room a faint glow or *phosphorescence* can be seen. To prevent oxidation, phosphorus is always kept under water. In oxygen, phosphorus burns with dazzling brilliancy. Heated to a temperature of  $250^{\circ}C$ . without access to air, or upon exposure to sunlight, it changes to *red phosphorus*.

2. *Red phosphorus*. This form of phosphorus is a dark red powder. It is slightly more than twice as dense as water. It is insoluble in water or in carbon disulfide.

Red phosphorus is not poisonous; it does not take fire when exposed to the air; its kindling temperature is about  $250^{\circ}C$ ., phosphorus pentoxide being formed as it burns. When heated without access to air to a temperature of about  $290^{\circ}C$ ., it sublimates and forms yellow phosphorus upon condensation.

**380. Uses.** Some phosphorus is used as a poison for rats, mice, and other vermin. Great care must be taken to see that food is not contaminated by such poisons. Small quantities of phosphorus find use in making special alloys with copper and tin. *Phosphor bronze* is not corroded by water, or by sea water.

During the World War, phosphorus was used in explosive shells and hand grenades that were designed for incendiary purposes. Incendiary bullets were effective in igniting the hydrogen in the gas bags of zeppelins, thus destroying them or bringing them down. Tracer bullets also contained phosphorus. The path they take is marked by the burning phosphorus, and a faulty aim may be corrected. The dense,



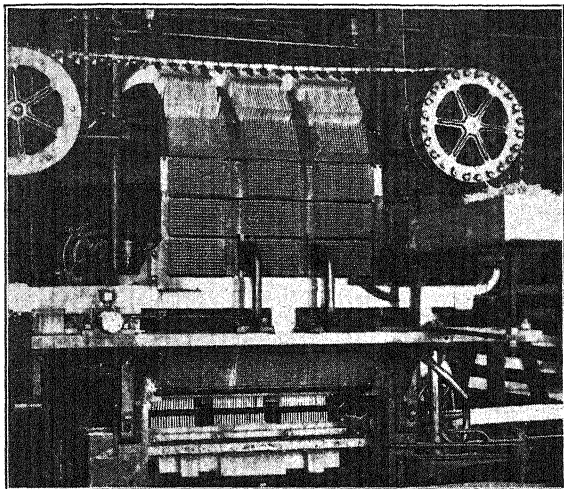
white clouds formed by burning phosphorus formed most effective smoke screens. But the bulk of the phosphorus finds use in making *matches* or in the manufacture of *fertilizer*.

**381. The Match Industry.** Two types of matches are in common use: (1) The "friction" match, which can be ignited by rubbing on any rough surface; and (2) the "safety" match, which is ignited by rubbing on a prepared surface.

1. *The "friction" match.* The early *friction* matches contained some phosphorus, and they were so easily kindled that many fires resulted from their use. Then, too, small children were sometimes poisoned by sucking the heads from such matches. The workmen in such match factories suffered from a disease which produced a decay of the jawbones. This disease, which usually attacked the jawbones through decayed teeth, was caused by the inhalation of phosphorus vapor. In 1913 a law was passed imposing a prohibitive tax (2¢ per 100 matches) upon the old phosphorus match. Their use is forbidden in most civilized countries.

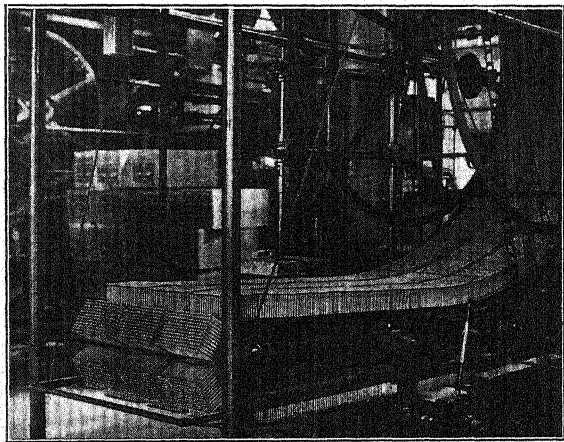
The modern friction match has a head composed of two parts. The larger portion consists of a paste containing glue, a filler, some coloring matter, and some oxidizing agent such as potassium chlorate or lead dioxide. By means of machinery, the sticks are dipped into this paste. Figures 220 to 222 show the various steps in the making of matches. The smaller portion, or the tip, of the head consists largely of *phosphorus sesquisulfide*,  $P_4S_3$ . This compound is quite as satisfactory as ordinary phosphorus, and it is non-poisonous.

2. *The "safety" match.* The head of the ordinary *safety* match contains antimony trisulfide,  $Sb_2S_3$ , glue, and some oxidizing agent. The box is covered with a layer of red phosphorus, powdered glass, and glue. Such matches do not ignite easily unless they are rubbed on the preparation on the box itself. The wood for the match sticks is often dipped into a solution of some fireproofing chemical, such as



*Courtesy The Diamond Match Co.*

FIG. 220. — Cutting matches and setting them in plates of automatic match machines.



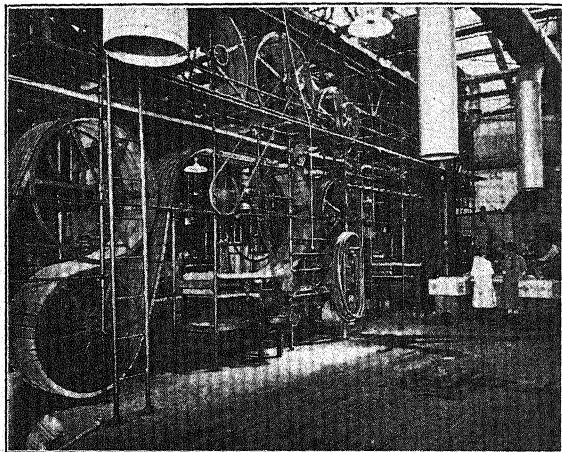
*Courtesy The Diamond Match Co.*

FIG. 221. — Dipping the matches into the paste to put on the tips.

ammonium phosphate. This prevents after-glow, and lessens the danger from fires due to careless handling of matches.

**382. How Phosphate Rock Is Made Useful for Fertilizers.**

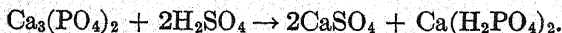
Plants and animals both need phosphorus. Plants get their phosphorus from the soils, but animals obtain theirs from plants. Most soils contain some phosphorus compounds, but by continual cropping, they may become deficient. To



*Courtesy The Diamond Match Co.*

FIG. 222. — Drying the matches on a long endless chain.

supply such deficiency, phosphates obtained from *guano*, *fish scrap*, *ground bone*, or *rock phosphate* may be added. But rock phosphate is insoluble in water, and slowly soluble in soil acids, so it should be made into a soluble form to make it available for plant use. Mineral matter dissolved in soil water can be taken in through the root-hairs of plants. Hence, rock phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , is treated with enough sulfuric acid to form *calcium acid phosphate*,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , which is soluble in water. The equation follows:



This form of calcium acid phosphate and calcium sulfate is often called *super-phosphate of lime*. The calcium sulfate, which has some value as a fertilizer, is not separated from the calcium acid phosphate.

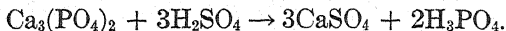
As a rule, not enough sulfuric acid is added to the rock phosphate to convert all the tri-calcium phosphate into the calcium acid phosphate. Then when the fertilizer stands in the bags, the two compounds slowly interact to form *reverted calcium phosphate*,  $\text{Ca}_2(\text{HPO}_4)_2$ . This compound is insoluble in water, but it dissolves slowly in water containing soil acids or carbon dioxide. Hence it has little value for immediate use as a fertilizer, but it is of value for the future. The equation follows:



The analysis printed on fertilizer bags often means little to the farmer. The following terms are used and per cents given: *total phosphoric acid*; *soluble phosphoric acid*; *insoluble phosphoric acid*; and *reverted phosphoric acid*. As a matter of fact, the fertilizer does not contain phosphoric acid as such, but there are phosphates of different kinds which would yield the per cent of phosphoric acid specified, if they were converted into phosphoric acid. For example, there may be enough of all the phosphates to be equivalent to 20% total phosphoric acid. There may be enough calcium acid phosphate to be equivalent to 16% of soluble phosphoric acid. There may be some tri-calcium phosphate and some reverted calcium phosphate.

★ 383. **The Oxides of Phosphorus.** Two oxides of phosphorus are known: *Phosphorus pentoxide*,  $\text{P}_2\text{O}_5$ , is a white solid formed when phosphorus burns in air or oxygen. It is the anhydride of phosphoric acid,  $\text{H}_3\text{PO}_4$ . Its great affinity for water makes it useful for drying gases. *Phosphorus trioxide*,  $\text{P}_2\text{O}_3$ , is formed when phosphorus burns in a limited supply of air. It is the anhydride of phosphorous acid,  $\text{H}_3\text{PO}_3$ .

★ **384. The Acids of Phosphorus.** Of several acids of phosphorus, *ortho-phosphoric acid*,  $\text{H}_3\text{PO}_4$ , is the most important. It may be prepared from its anhydride, but it is usually prepared by treating calcium phosphate with sulfuric acid.



*Phosphorous acid*,  $\text{H}_3\text{PO}_3$ , *pyrophosphoric acid*,  $\text{H}_4\text{P}_2\text{O}_7$ , *metaphosphoric acid*,  $\text{HPO}_3$ , and *hypophosphorous acid*,  $\text{H}_3\text{PO}_2$ , are best known through the usefulness of some of their salts.

★ **385. The Salts of the Acids of Phosphorus.** Phosphoric acid is a tri-basic acid, and it can form three classes of salts. To illustrate, *tri-sodium phosphate* has the formula  $\text{Na}_3\text{PO}_4$ ; *di-sodium phosphate* has the formula  $\text{Na}_2\text{HPO}_4$ ; and *mono-sodium phosphate* has the formula  $\text{NaH}_2\text{PO}_4$ . These salts show that phosphoric acid may yield the following ions:  $\text{PO}_4^{=}$ ,  $\text{HPO}_4^{-}$ , and  $\text{H}_2\text{PO}_4^{-}$ . Certain phosphates and hypophosphites are used in medicine. Ammonium phosphate is used for fire-proofing. Tri-sodium phosphate is used as a water softener, and in washing powders. Mono-calcium phosphate finds use in making baking powder.

## B. ARSENIC

**386. How Arsenic Occurs in Nature.** Some arsenic is found uncombined in nature. It is found in many sulfide ores, and as an impurity associated with the ores of other metals, such as copper and iron.

**387. Preparation and Properties of Arsenic.** In smelting such ores as copper, the arsenic is converted into an oxide,  $\text{As}_2\text{O}_3$ . This oxide is volatile and may escape into the air and settle on foliage and grass. Cattle and sheep have been poisoned in this manner. This compound, which at one time was considered a nuisance and caused many damage suits, is now precipitated in the stacks of the smelters and converted into a valuable insecticide.

Metallic arsenic is a brittle gray solid with a metallic

luster. Chemically it may act like a metal and form oxides and chlorides, but it more often acts as a non-metal and forms acids analogous to those of phosphorus. When heated in the air it burns with a blue flame and forms *arsenious oxide*,  $\text{As}_2\text{O}_3$ , a volatile compound that has an odor like garlic. This oxide is commonly called *white arsenic*. Arsenic unites with nascent hydrogen to form *arsine*,  $\text{AsH}_3$ , a compound analogous to ammonia. It is extremely poisonous.

**388. Uses of Arsenic and Its Compounds.** Metallic arsenic is little used. When a small percentage is added to

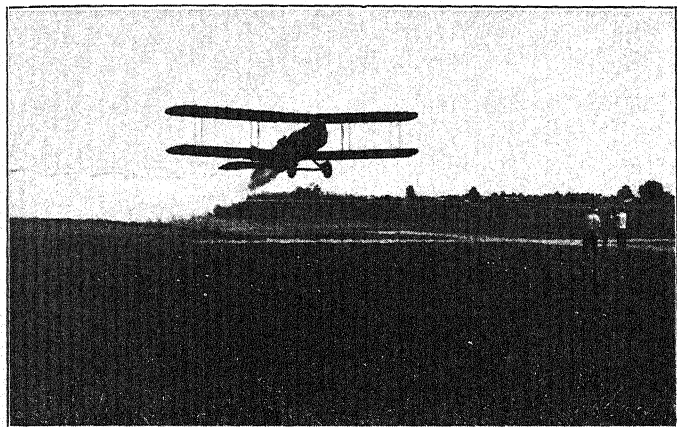


FIG. 223. — Using an airplane to spray cotton fields with calcium arsenate.

lead in making shot, it makes the shot harder and more nearly spherical. The *tri-oxide*,  $\text{As}_2\text{O}_3$ , finds use in making other compounds of arsenic, in the manufacture of glass, and as a preservative of the skins used by taxidermists for mounting. Several medicines contain small quantities of arsenic. Some of the compounds of arsenic form beautiful pigments, but they are so volatile that they are very dangerous.

Arsenic is used very extensively in making insecticides. Paris green, a compound of arsenic and copper, is an

example. London purple is another example. Enormous quantities of *lead arsenate*,  $Pb_3(AsO_4)_2$ , are used every year for spraying fruit trees and shade trees to destroy such noxious insects as the caterpillars of the gypsy moth and the brown-tail moth, and the larvae that attack our fruits. Airplanes are used to spray the cotton fields in our southern states to keep in check the cotton-boll weevil. *Calcium arsenate*,  $Ca_3(AsO_4)_2$ , is used for this purpose. (See Fig. 223.)

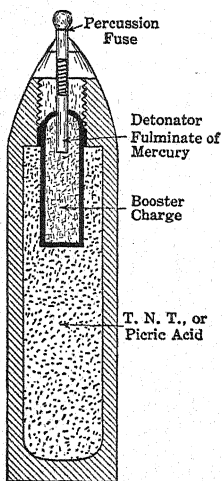


FIG. 224. — Shell filled with explosive.

Arsenic compounds were used during the World War to make poison gases and "sneeze gases." *Di-phenyl-chlor-arsine*, for example, was embedded in the T. N. T. of a high explosive shell. (See Fig. 224.) When the explosion occurred, small particles of this compound were scattered in all directions. The particles penetrated the gas masks and caused violent sneezing. Thus they forced the removal of the gas masks, and left the men unprotected against more poisonous gases.

### C. ANTIMONY

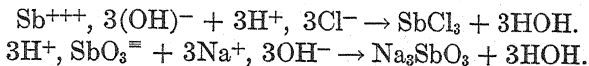
**389. How Antimony Occurs in Nature.** Antimony occurs free in nature. It is also found as *stibnite*, a sulfide of antimony,  $Sb_2S_3$ , an ore that is widely distributed. In the United States, it is obtained from "antimonial lead" ores.

**390. Properties.** Antimony is a silver-white element with a bright metallic luster; it is fairly dense and very brittle. It is less active chemically than arsenic, but when it is heated in the air it forms the tri-oxide,  $Sb_2O_3$ , a white volatile solid. Antimony is not affected by hydrochloric acid, but it dissolves slowly in *aqua regia* and forms antimony tri-



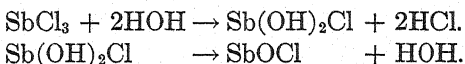
chloride,  $\text{SbCl}_3$ . Like arsenic, it forms a series of weak acids.

★ The hydroxide of antimony is an excellent example of a compound that is *amphoteric*; in the presence of a strong acid it acts as a base. In the presence of a strong base it behaves as an acid. The following ionic equations show how it ionizes in different ways under different conditions:



In the first case, the base-forming antimony forms antimony tri-chloride. In the second case, *antimonious acid* forms sodium *antimonite*. Many hydroxides behave in a similar manner.

When we try to dissolve antimony tri-chloride in water, hydrolysis first occurs, and then the basic chloride that is formed loses water and forms a new type of compound, *antimony oxy-chloride*,  $\text{SbOCl}$ ; it is sometimes called the *sub-chloride*. The two equations represent the successive reactions:



In making a solution of antimony tri-chloride in the laboratory, we add some concentrated hydrochloric acid to the water solution. Thus we increase the concentration of the hydrogen ion and prevent the hydrolysis. This is an excellent example of mass action.

**391. Nature of Alloys.** By melting together two or more metals a substance called an *alloy* is often formed. In some cases an alloy appears to be merely a mixture of metals; in other cases a compound appears to be formed, since the proportion is definite. Many of the alloys are *solid solutions* of metals in one another. When such alloys are cooled, crystals of one of the metals may separate. Figure 225 shows a photo-micrograph of an alloy of antimonial lead. Crystals of antimony may be seen embedded in the metallic lead.



An alloy may have properties quite unlike those of any of its constituents, or in some cases they may be intermediate. Usually the melting point of an alloy is lower than the average melting point of its constituents, and often it is below that of any one of them.

**392. Uses of Antimony.** Antimony is used in preparing several alloys. *Type-metal* contains antimony, lead, and tin; the antimony is especially important since it expands when it solidifies, and the type is thus made distinct and clear-cut. Antimony is also used in the non-friction alloys such as *Babbitt's metal*, or *lead and antimony*. *Britannia metal*, an alloy much used in making table-



FIG. 225. — Antimonial lead. Magnified 75 diameters.

ware, is an alloy of antimony, tin, copper, and often zinc. Finely divided antimony, under the name of *antimony black*, is used for coating plaster casts to give them a metallic appearance.

The *sulfides of antimony* are used as pigments. They also find use in vulcanizing rubber. Red rubber contains antimony tri-sulfide,  $\text{Sb}_2\text{S}_3$ . *Tartar emetic* is a compound of antimony that is used as a mordant in the dyeing of cotton goods.

#### D. BISMUTH

**393. Bismuth.** Bismuth is a heavy metal that resembles antimony to a considerable extent. It has a distinctly reddish hue. It is more metallic than antimony and forms bases more readily.

The chief use of bismuth is in the manufacture of the *fusible* alloys. Two common ones, Wood's metal and Rose's metal, melt at temperatures below that of boiling water. The fusible alloys are used as safety plugs in boilers, as fuses in electric wiring, in fire alarms and automatic sprinkling devices, and for automatically closing the doors of fireproof safes. (See Fig. 226.)

Bismuth acts as a trivalent element in the formation of most of its compounds. It acts in the same manner as antimony when its salts are treated with water, hydrolysis first occurring, and then dehydration. Thus the chloride,  $\text{BiCl}_3$ , forms an *oxy-chloride*, or *sub-chloride*,  $\text{BiOCl}$ , when treated with water. The sub-nitrate is used in medicine. When it is mixed with barium sulfate and suspended in buttermilk, it may be given to patients who are to have X-rays taken of the digestive tract. Such a suspension is moderately opaque to X-rays, and the whole digestive tract appears darker by contrast than the other parts of the body.

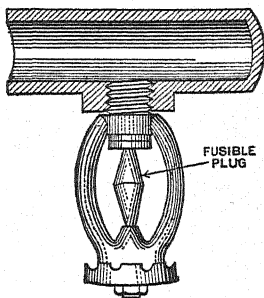


FIG. 226. — Automatic sprinkler.

## SUMMARY

The nitrogen family consists of five elements: *nitrogen*, *phosphorus*, *arsenic*, *antimony*, and *bismuth*. The group valence is 3 or 5.

Phosphorus occurs in nature as *calcium phosphate*. It is extracted by heating the calcium phosphate with sand and coke in an electric furnace.

Of the allotropic forms of phosphorus, the *white* variety and the *red* are the most common. *White* phosphorus is active, even at room temperature. It burns with a hot flame, forming phosphorus pentoxide. *Red* phosphorus is inactive at low temperatures.

Phosphorus is used in making *alloys*, in the *match* industry, as a *poison*, and in *fertilizers*. To make calcium phosphate available for use as a fertilizer, it is treated with sulfuric acid. This gives *mono-calcium phosphate*, which is water soluble.

*Arsenic* is used for hardening shot. Its compounds find use in medicines, for pigments, and as insecticides.

*Antimony* is used in such alloys as: *type-metal*, *Babbitt's metal*, and *Britannia metal*.

*Bismuth* is used in the manufacture of fusible alloys; its salts are used in medicine.

The following tabular form shows the rather close relationship between the elements of the nitrogen family:

	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic weights...	14	31	75	120	209
Valence.....	3, 5 In oxides some of the elements have a valence of 1, 2, or 4	3, 5	3, 5	3, 5	3, 5
Hydrides.....	NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>	SbH <sub>3</sub>	
Oxides.....	N <sub>2</sub> O <sub>3</sub> N <sub>2</sub> O <sub>5</sub>	P <sub>2</sub> O <sub>3</sub> P <sub>2</sub> O <sub>5</sub>	As <sub>2</sub> O <sub>3</sub> As <sub>2</sub> O <sub>5</sub>	Sb <sub>2</sub> O <sub>3</sub> Sb <sub>2</sub> O <sub>5</sub>	Bi <sub>2</sub> O <sub>3</sub> Bi <sub>2</sub> O <sub>5</sub>
Acids.....	HNO <sub>2</sub> HNO <sub>3</sub>	H <sub>3</sub> PO <sub>2</sub> H <sub>3</sub> PO <sub>4</sub>	H <sub>3</sub> AsO <sub>3</sub> H <sub>3</sub> AsO <sub>4</sub>	H <sub>3</sub> SbO <sub>3</sub> H <sub>3</sub> SbO <sub>4</sub>	
	Very strong acids	Weak acids	Weak acids	Very weak acids	Basic

## QUESTIONS

### GROUP A

1. Why have laws been passed in many countries forbidding the use of white phosphorus for making matches?
2. If a solution of phosphorus in carbon disulfide is poured on a piece of filter paper, spontaneous combustion takes place as soon as the disulfide evaporates. Explain.
3. How does the strength of the acids in this family vary with the atomic weights? How does it vary with the valence?
4. Why should the analysis of a fertilizer show the per cent of each phosphate present as well as the total amount?

5. How do you account for the fact that antimony and bismuth occur free in nature while phosphorus never does?
6. How should white phosphorus be stored? What precautions should be taken in handling white phosphorus?
7. Explain how fusible alloys are used with fire-doors. How does a fusible plug protect a steam boiler in an ordinary furnace?
8. How does a friction match differ from a safety match?
9. Explain the action of the automatic water sprinkler in extinguishing fires.
10. Why is phosphorus essential to animal life? Where do we get our phosphorus?
11. In what ways are the elements of the nitrogen family useful to the farmer?

## GROUP B

12. How could you prepare red phosphorus from the white? How could you prepare white phosphorus from the red?
13. Under what circumstances does the hydroxide of antimony act as a base? When does it act like an acid?
14. Why is the use of arsenic as a pigment in wall papers forbidden?
15. Write the formulas for three calcium phosphates. Write the formula for sodium arsenite; for sodium arsenate.
16. The anti-friction alloys maintain hard smooth surfaces when rubbed. Of what value are such metals?
17. From the electron theory, explain why the elements of the nitrogen family have a valence of 3 when they unite with hydrogen, but their valence is 5 when they combine with oxygen.

## SUPPLEMENTARY PROJECTS

Prepare a report on one of the following topics:

1. Marsh's test for arsenic.

Reference: RICHARDSON, LEON B., *General Chemistry*. Henry Holt and Co.

2. Anti-friction metals.

Reference: "Bearing metal," *Scientific American Supplement* 77, 242 (1914).

## CHAPTER 28

### THE CARBON-SILICON GROUP

#### Vocabulary

**Abrasive.** A hard substance used for cutting, grinding, or polishing.

**Infusible.** Referring usually to substances that can be melted with great difficulty.

**Extruded.** Forced out or pushed out.

**Infusoria.** An order of one-celled animals.

**Corrugated.** Folded or wrinkled into alternate ridges and grooves.

**Polymerization.** The union of two or more molecules of a substance to form a more complex molecule having a higher molecular weight.

**Plastic.** A substance that may be molded, blown, or pressed into almost any desired shape.

**394. Introductory.** Although there are several elements in this family, only two of them are of great importance. We have already studied carbon and its oxides. *Silicon*, Si, is similar in its chemical properties to the element carbon. Its oxides and acids are analogous. Both elements have a valence of 4. Carbon is sometimes found free or uncombined in nature, but silicon is never found native.

#### A. SILICON AND ITS COMPOUNDS

**395. Where Silicon Is Found.** Oxygen is the only element that is found more abundantly than silicon, which forms about 25% of the earth's crust. Few persons have ever seen the element itself, however, since it occurs in nature as *silica*, or silicon dioxide,  $\text{SiO}_2$ . The element may be isolated by heating sand, or silica, with carbon in an electric furnace. Sand, quartz, and a large number of silicate rocks are widely distributed in nature.

**396. Silica.** This is one of the most useful compounds of silicon. It occurs in the following forms:

1. *Sand* is the most common form of silica, and it is also one of the most useful. Large quantities of sand are used every year in the manufacture of *glass*. In several ways it is used as an *abrasive*. In the manufacture of sandpaper, a heavy paper is coated with glue, and sand is then sprinkled over the surface. A *sand-blast*, which is used for polishing and cutting very hard surfaces, makes use of a stream of sand driven at a high velocity. *Scouring soaps* or *powders* usually contain powdered soap, washing soda, and powdered silica, the latter substance being "gritty" enough to do the scouring work. Sand is also used extensively in making *mortar* and *concrete*, while considerable quantities are used for *lining molds*, into which molten iron is to be poured for making castings. It is especially suitable for this purpose since it is infusible and quite easily removed from the casting after it has solidified.

2. *Sandstone* differs from sand only in that the particles are held together by a kind of cement. Sandstone is used as a building material; it is also sawed into slabs and used for sidewalks or for making grindstones.

3. *Quartz* is a transparent, crystalline variety of silica. Quartz crystals are six-sided prisms surmounted at each end by six-sided pyramids, each crystal having 18 faces (see plate of crystals). While pure *rock crystal* is colorless, traces of impurities impart to it characteristic colors. For example, *amethyst*, *smoky quartz*, *rose quartz*, and *milky quartz* are all well-known varieties of quartz.

Quartz may be melted and fashioned into tubing, crucibles, and other laboratory apparatus. (See Fig. 227.) Such apparatus is not as easily acted upon by acids and alkalis as ordinary glassware; it has so low a coefficient of expansion that it may be heated red hot and then plunged into cold water without breaking. Quartz is also drawn into very fine threads to be used as suspension fibers in very delicate electrical instruments. A new method of fusing

quartz was recently developed by E. R. Berry, of the General Electric Company. Quartz is melted in a graphite crucible in an electric furnace and extruded from the furnace under high pressure. (See Fig. 228.) Quartz transmits ultra-violet

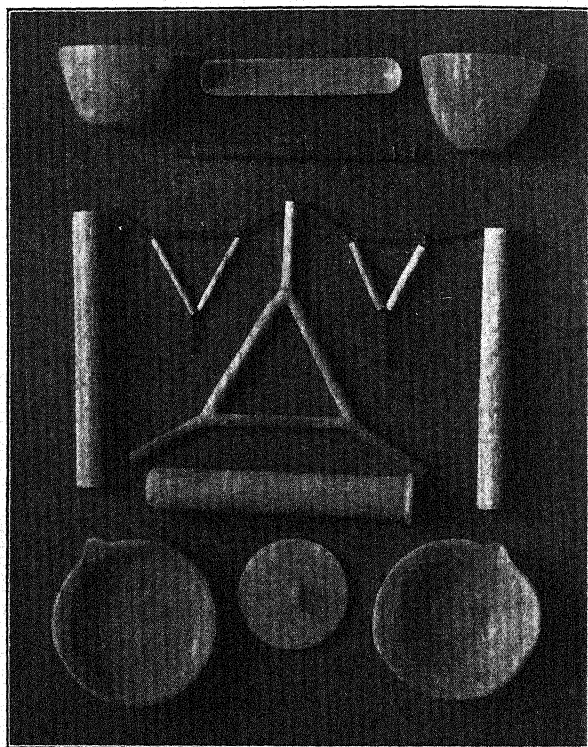


FIG. 227. — Silica ware.

rays much better than glass does. If it could be made cheap enough to be substituted for glass in our windows, one could get the beneficial effects of the sun's rays without going to the seashore.

4. *Amorphous silica* includes such common substances as



*flint, jasper, chalcedony, sard, carnelian, onyx, and agate.* The last two are made up of bands of different color. Fine specimens of crystallized and amorphous silica are used as semi-precious gems.

5. *Silica in plants and animals.* Practically all soils contain silica. To some extent silica is found in plants, especially in

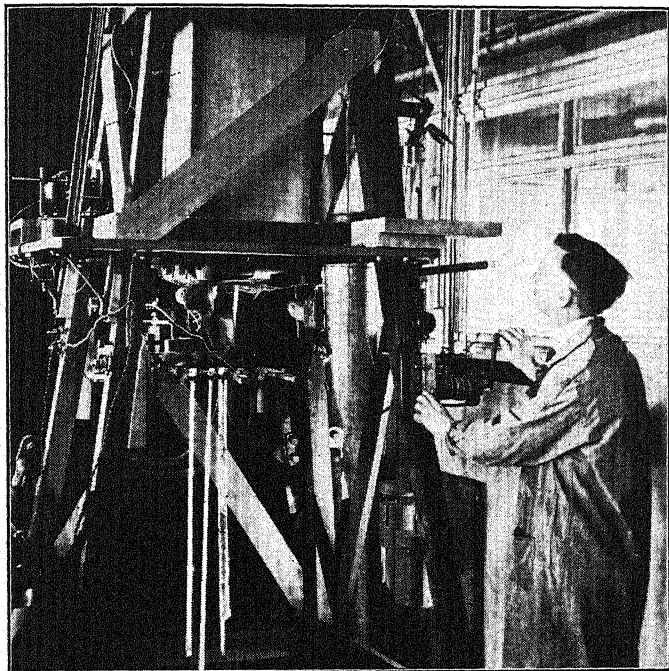


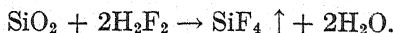
FIG. 228. — Electric furnace from which quartz is extruded.

the leaves and stems, where it appears to be useful in giving rigidity. Considerable silica is present in the ash formed by burning leaves and stems. Under certain conditions silica may replace the fibers of wood entirely and form *petrified wood*.

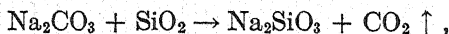


The bones of vertebrate animals are composed of calcium phosphate, but the skeletons of some one-celled marine animals contain silica. These animals belong to the order *infusoria*; the *diatoms* are common examples. Large areas of the ocean bottom, as well as extensive land areas, are covered with deposits of *infusorial*, or *diatomaceous* earth, consisting of the microscopic skeletons of these marine animals. Such material may be used as an adsorbent, as in the manufacture of dynamite by the adsorption of nitroglycerine. As a silver polish, it is sold under the name of *electro-silicon*. Silica is present in the hair, nails, and horns of animals.

**397. Properties of Silica.** Silicon dioxide is a hard solid; it can be fused only at very high temperatures. It is insoluble in water and the ordinary acids. Hydrofluoric acid acts upon it as shown by the equation,

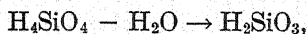


The *silicon tetra-fluoride*,  $\text{SiF}_4$ , that is formed is volatile and escapes into the air. The strong alkalis attack silica and form silicates. Sodium carbonate reacts with silica and forms sodium silicate. The equation,



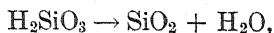
represents one of the reactions that occur in making glass.

★ **398. Silicic Acids.** There are many acids of silicon, but they are not important compounds. Many of their salts are found in nature. Since silicon has a valence of 4, it is possible to have an acid formed that has the formula  $\text{H}_4\text{SiO}_4$ . This acid is called *ortho-silicic acid* (*orthos*, "straight"). If this acid is partially dehydrated, as shown by the equation,



*meta-silicic* acid is formed. An acid formed by dehydrating, or partially dehydrating, another acid in the same series is

called a "*meta*" acid. Heating meta-silicic acid forms silicon dioxide,



which *appears* to be the anhydride of silicic acid. It is impossible, however, to hydrate silicon dioxide and form the acid. The silicic acids are all very weak acids.

**399. Silicates.** The silicates of sodium and potassium are the only ones that are soluble. Their water solution is known as *water glass*. Sodium silicate has the formula  $\text{Na}_2\text{SiO}_3$ . It finds use as a filler in laundry soaps, for making casts and artificial stone, as a binder in abrasive wheels and furnace linings, for sizing walls, for fire-proofing materials, and as an adhesive in making wall-boards and corrugated paper boards for cartons. When eggs are dipped into a solution of water glass, the pores of the egg become filled with silicates, and bacteria cannot get through to cause decomposition. Hence water glass is suitable for preserving eggs.

Silicates that are found in nature include such well-known substances as *clay*, *asbestos*, *talc* or *soapstone*, *feldspar*, *granite*, *garnets*, *slate*, *shale*, and *pumice stone*. These silicates find extensive use in making cement and pottery, and in the building industries. The *alberene* used for laboratory sinks and wash tubs is made from talc. Talc is also ground to a fine powder and sold as *talcum powder*. French chalk used by tailors has the same composition.

★ Many of the silicates found in nature contain such radicals as  $(\text{SiO}_3)^{-2}$ ,  $(\text{SiO}_4)^{-4}$ ,  $(\text{Si}_2\text{O}_7)^{-6}$ ,  $(\text{Si}_3\text{O}_{11})^{-10}$ , etc. They seem to be salts of *associated* molecules of silicic acid. For example,  $2\text{H}_4\text{SiO}_4 \rightarrow \text{H}_8\text{Si}_2\text{O}_8$ ; or,  $3\text{H}_4\text{SiO}_4 \rightarrow \text{H}_{12}\text{Si}_3\text{O}_{12}$ . The first is called *di-silicic acid*, and the second is known as *tri-silicic acid*. Such association of molecules is known as *polymerization*. They lose water readily and form radicals of the types given above. Such radicals can combine with metallic ions to form mixed silicates of great complexity.

For example,  $(\text{Si}_3\text{O}_{11})^{-10}$ , might unite with two trivalent metallic ions, one bivalent metallic ion, and two univalent metallic ions.

400. "Carborundum,"  $\text{SiC}$ . This interesting compound may be considered as a carbide of silicon, or as a silicide of

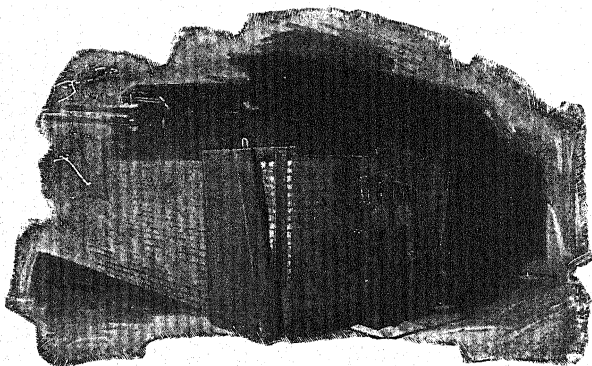


FIG. 229. — Electric furnace for making carborundum.

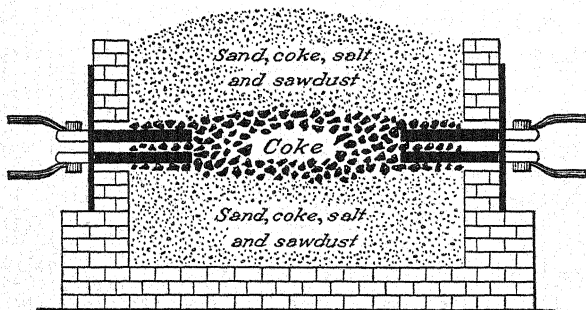


FIG. 230. — Sectional view of an electric furnace for making carborundum.

carbon. It is made by heating sand and coke in an electric furnace. (See Fig. 229.) Salt is usually added to the mixture to facilitate fusion, and sawdust to make it more porous. (See Fig. 230.) "Carborundum" is a crystalline com-

pound of extreme hardness. It is one of the hardest compounds made artificially. Hence it is an excellent abrasive. It is extensively used for grinding and polishing metals.

*Crystolon* is an abrasive that is made in much the same manner as "Carborundum." It is made into hones, grinding wheels, and polishing cloths. (See Fig. 231.)

## B. GLASS MANUFACTURE

401. What Is Glass? As early as 4000 B.C., the Egyptians knew how to make glass, one of our most useful plastics.

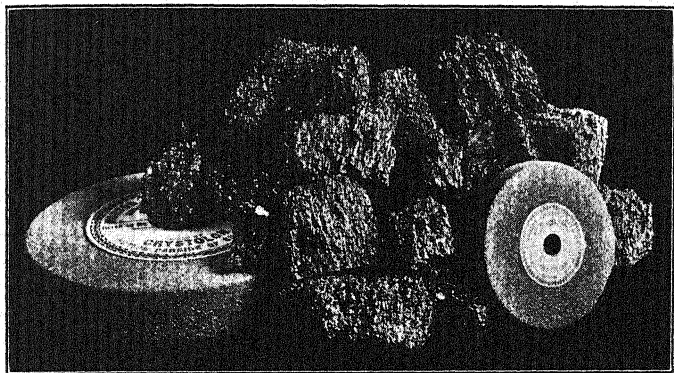


FIG. 231. — Crystolon abrasives.

Although glass is hard and quite brittle when cold, yet it softens when heated and becomes so plastic that it can be blown, rolled, or pressed into any desired shape. Many of its uses depend upon the fact that it is insoluble in water and that it is transparent. Chemically *ordinary glass is made up of the silicates of sodium and calcium*. It is often spoken of as a mixture of these compounds, but it is probably a solid solution of these silicates in each other. Potassium may be substituted for the sodium, and lead, barium, aluminum, or zinc may take the place of all or part of the calcium.

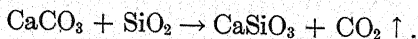
**402. How Is Glass Made?** 1. *Raw materials.* In making ordinary glass the raw materials, *sand*, *limestone* ( $\text{CaCO}_3$ ), and *sodium carbonate* ( $\text{Na}_2\text{CO}_3$ ) are heated in a pot of fire clay for about 24 hours. The heating is continued until the gases, mainly carbon dioxide, are liberated. The impurities



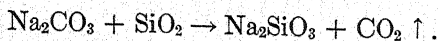
*Courtesy of Corning Glass Works*

FIG. 232. — Making a large tub from pyrex glass.

are removed by skimming. Some of the sand unites with the limestone as represented by the equation:



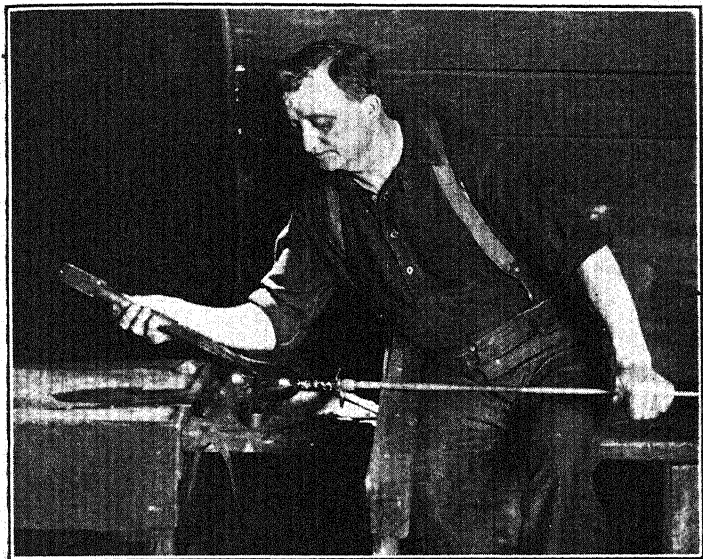
The rest of the sand unites with the sodium carbonate:



2. *How glass is worked.* In making what is called *hand-blown* glass, a workman introduces into the furnace one end of a blowpipe about six feet long and rolls it around until a sufficient amount of glass adheres to it. He then blows a large bubble in the glass and brings it to the desired shape by swinging it, rolling it on a hot plate, or blowing it in a mold.

(See Fig. 232.) Various tools are used in shaping and finishing the hand-blown products. (See Fig. 233.)

*Bottles* may be blown in molds and then finished by the use of a special tool to shape the neck and remove the sharp edges. (See Fig. 234.) Many of the bottles now used are blown in special bottle-making machines. (See Fig. 235.)



*Courtesy of Corning Glass Works*

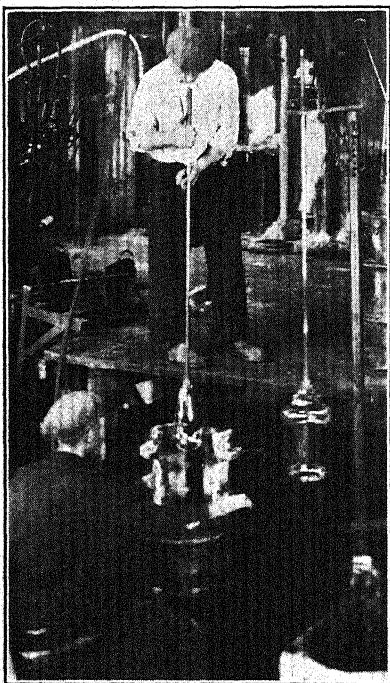
FIG. 233. — Flaring out the edge in making table glassware.

In the most modern method of making *plate glass*, the product is drawn continuously from the tank. It then passes directly through the annealing, grinding, and polishing processes. (See Figs. 236 and 237.)

Not many years ago window glass was hand blown into large cylinders which were then cut along one side and flattened out. Then larger cylinders were blown by the use of compressed air. Now large quantities of window glass



are made by drawing the glass vertically in flat sheets. In one process the glass is drawn from a slot in a clay form which floats on the surface of the molten glass. (See Figs. 238, 238a, and 238b.)



Courtesy of Corning Glass Works

FIG. 234. — Blowing a glass bottle in a mold. Bottle shown at right.

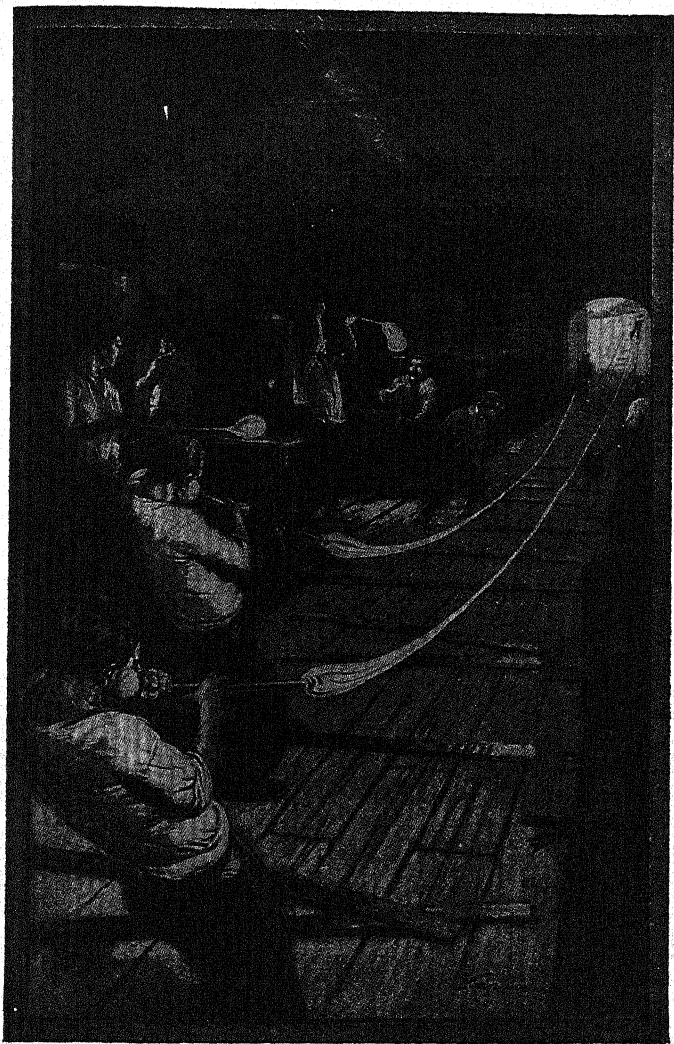
Cheap *glass dishes* are sometimes made by pressing the glass into a mold which imparts to the glass the desired design. *Cut glass* is molded and then stamped with the design. It is then cut by means of an abrasive wheel and polished with rouge, or iron oxide.

3. *Annealing*. If glass cools quickly, it becomes brittle. To make a tougher glass, it is annealed by cooling it slowly. This process is accomplished by passing the glass through a *lehr*, or oven, hot at one end and cool at the other,

in which it is cooled gradually. (See Fig. 238c.)

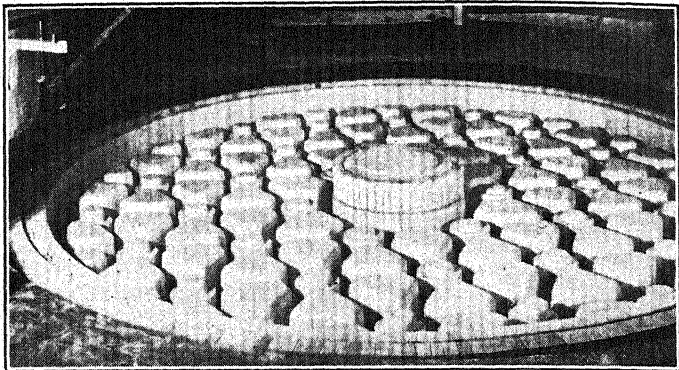
**403. Kinds of Glass.** 1. *Soda-lime glass*. Ordinary window glass is made from washing soda, limestone, and sand. Traces of iron in the sand impart to the glass a green color. *Crown glass*, used for lenses, is made by decolorizing such glass.

2. *Potassium-lime glass*. By using potassium carbonate instead of sodium carbonate, one gets a harder glass that



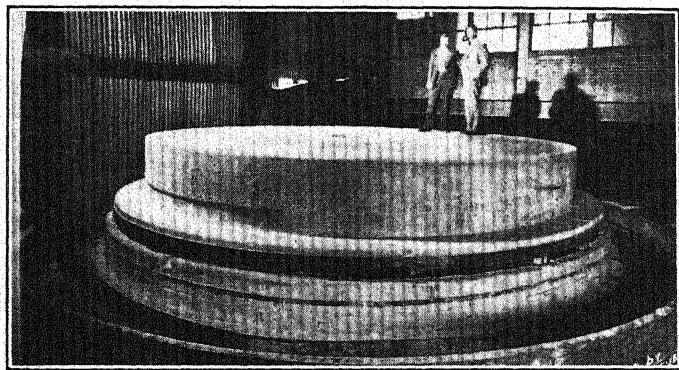
· Making glass tubing by hand is gradually being superseded by machine methods. Glass is supplied continuously from the furnace to a rotating mandrel from which the glass is pulled by a machine some 150 ft. distant. Such a machine can make over 100 miles of small tubing per day and cut it up into 4- or 5-ft. lengths. The old process shown in this illustration is a fascinating one to watch.



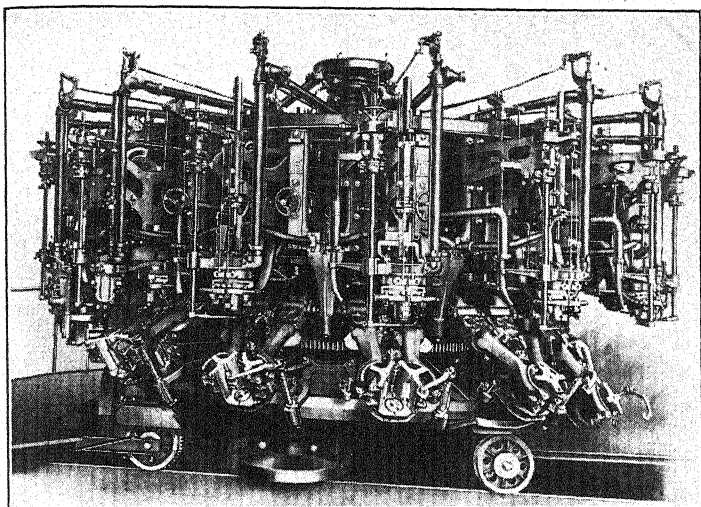


*Courtesy Corning Glass Works*

The assembled mold for receiving the glass to make the 200-inch disc for the world's largest telescope. The central core will produce a 40-inch hole in the center of the disc to be used in its mounting. To insure proper cooling and the removal of blisters, the mold was heated before the glass was poured into it.



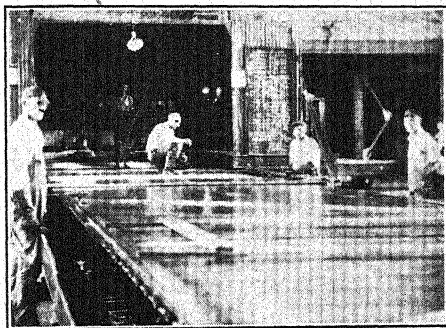
This large disc of glass was made at Corning, New York, for use in a new telescope for the California Institute of Technology. It is 200 inches in diameter, more than two feet thick. Its weight is 20 tons. When cooled and polished, this huge disc should bring heavenly bodies to a distance only one-fourth that ever attained before by the use of a telescope.



*Courtesy of Owens-Illinois Glass Co.*

FIG. 235. — Bottle-blowing machine.

has a higher melting point. Because it is not so easily affected by alkalis, it is known as "resistance" glass. During the World War our supply of hard glass, which came from Germany, was cut off. Our manufacturers were forced to develop a similar glass without the use of potassium. They succeeded in making a superior product

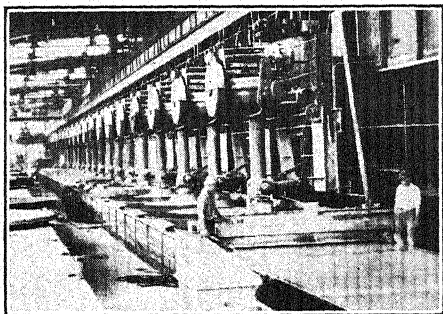


*Courtesy of Pittsburgh Plate Glass Co.*

FIG. 236. — The finished rough glass as it leaves the Lehr.

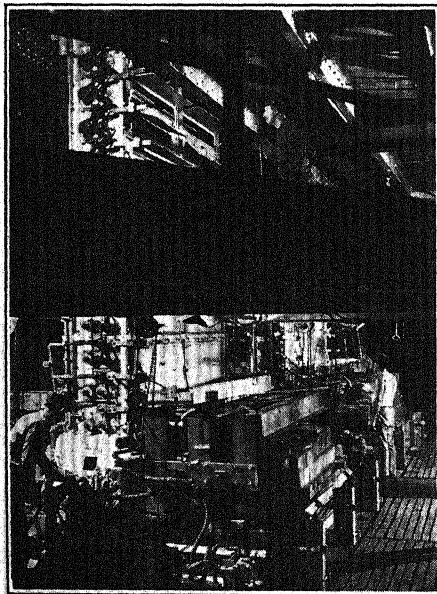
for laboratory use, a glass of low coefficient of expansion.

3. *Pyrex glass* is made by fusing silica, borax, and alumi-



*Courtesy of Pittsburgh Plate Glass Co.*

FIG. 237. — Grinding and polishing plate glass.



*Courtesy of Pittsburgh Plate Glass Co.*

FIG. 238. — Machine for making flat window glass.

num oxide. It is hard, not easily fused, and it resists the action of alkalis. It has such a low coefficient of expansion that it is very suitable for making baking dishes. In the laboratory, too, there is little loss on account of breakage, if pyrex glass is used.

#### 4. *Flint glass.*

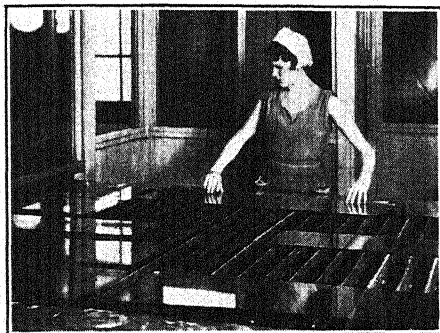
Lead added to glass makes it soft and lustrous; it also increases its index of refraction. Hence it finds use in making cut glass, in lenses for optical work, and for crystals. It is more brilliant than ordinary glass, and when properly cut, it gives an excellent play of colors.

#### 5. *Reinforced glass.*

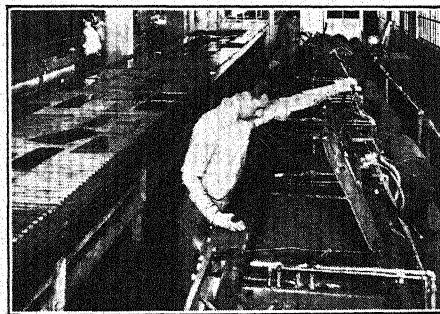
To strengthen glass, a net-work of wire may be embedded in the glass while it is still plastic. Non-



The girl in the foreground is cutting pyroxyline sheets into the size used for the Duplate glass. In this room, too, the pyroxyline is inspected for defects. It must contain, too, only a specified amount of moisture. If it is too dry, it is hung in a humidifying room. If too moist, it goes to the drying room.

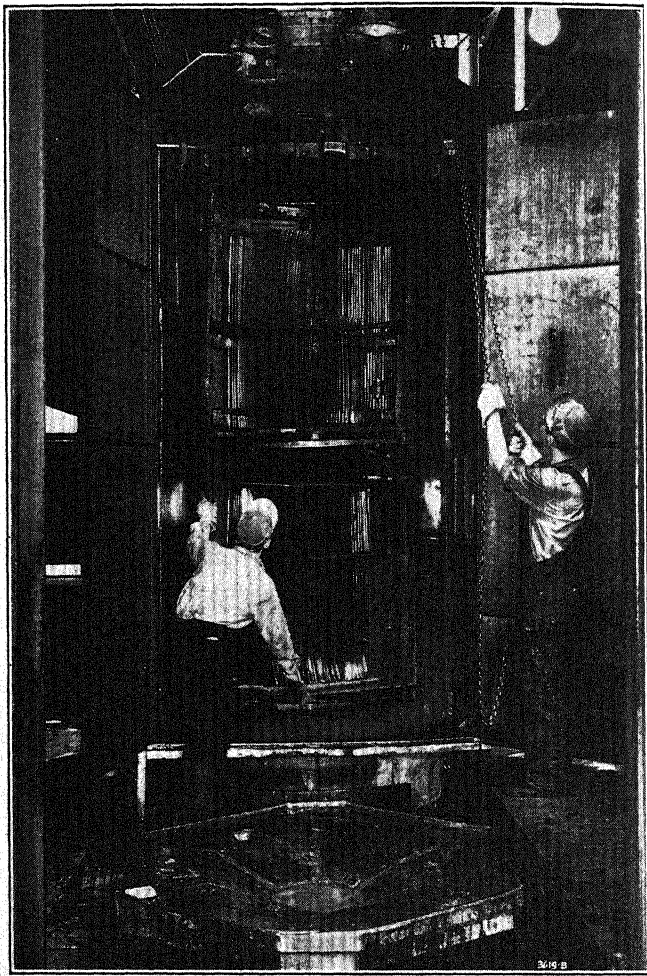


The operator is here seen placing the sheet of pyroxyline between two pieces of polished plate glass. The cleaned and cemented surfaces of the glass are placed next to the pyroxyline. Both surfaces of the pyroxyline must be thoroughly washed before this operation, which completes the making of the sandwich.



Here we see the assembled glass sandwiches as they move along a traveling belt from the assembly room. At the right they receive the preliminary pressing. The Duplate is covered with rubber, the air is then removed and the press closed. For four minutes a pressure of 80 lb. per sq. in. and a temperature of 190° F. are maintained.

*Courtesy of Pittsburgh Plate Glass Co.*



*Courtesy Pittsburgh Plate Glass Co.*

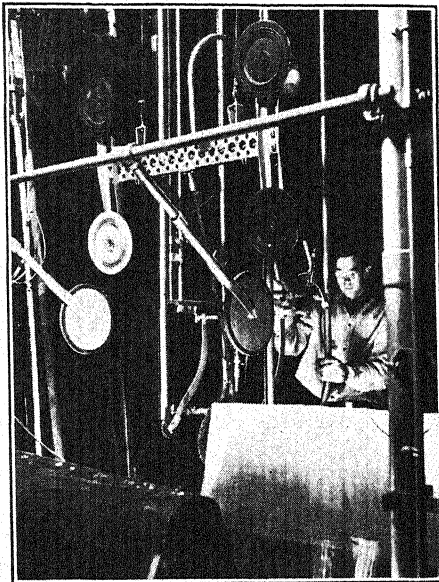
The sandwich glass is shown entering the pressure chamber. Under high pressure the two plates of glass and the sheet of *Pyroxyline* are pressed into a solid piece.



shatter glass, whose use in automobile windows and windshields is now required in some states, is made by cementing glass to both sides of a transparent sheet of pyralin or pyroxyline. *Duplate* and *triplex* glass are in common use. (See the series of illustrations shown opposite page 468.)

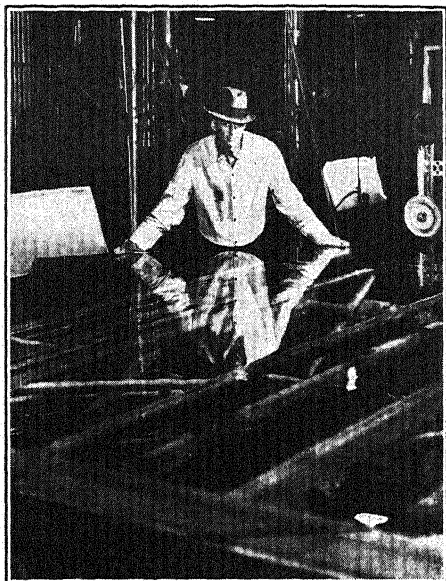
**404. Color in Glass.** The sand from which glass is made usually contains some iron. This metal imparts to the glass a green color. This color is rather an advantage in fruit jars, and in some bottles, but it is undesirable for window glass or for optical glass. It may be neutralized by adding a certain amount of *manganese*. An excess of manganese imparts to the glass a violet

or purplish color. A trace of chromium in glass gives a clear green color. Cobalt gives a blue color; carbon, sulfur, or silver will give a yellow color to glass. Selenium is used to impart to glass the red color needed for signal lights or for the tail-lights of automobiles. For making white glass, or opalescent glass, either calcium fluoride or cryolite is added. It takes only a small quantity of the metal in each case to color a large batch of glass.



Courtesy of Pittsburgh Plate Glass Co.

FIG. 238a. — The glass is handled at top of machine by suction discs. Vacuum cups serve as fingers.



*Courtesy of Pittsburgh Plate Glass Co.*

FIG. 238b. — Cutting glass into squares.



*Courtesy of Corning Glass Works*

FIG. 238c. — Baking dishes of pyrex glass coming from the annealing oven.



## SUMMARY

The most important elements in the carbon family are *carbon* and *silicon*.

*Silica* has the formula  $\text{SiO}_2$ ; it occurs in nature as sand, sandstone, the several varieties of quartz, and amorphous varieties such as flint, jasper, agate, and onyx. Silica is also found in plants and some animals. Fused silica finds use in the manufacture of laboratory apparatus.

Several acids of silicon are known. Their salts are called *silicates*. *Talc*, *mica*, *asbestos*, *clay*, *granite*, *feldspar*, and *pumice stone* are important silicates that are found in nature.

"Carborundum" is a carbide of silicon. It finds extensive use as an abrasive.

*Glass is a solid solution of two or more silicates.* Ordinary glass is made of sand, sodium carbonate, and limestone. Potassium carbonate is sometimes substituted for the sodium carbonate. Compounds of aluminum, boron, or lead may be substituted for part or all of the calcium carbonate.

Crown glass, flint glass, Bohemian glass, and pyrex glass are some of the most important kinds of glass. Various metallic oxides are added to the melted glass to impart certain colors to it.

## QUESTIONS

## GROUP A

1. Summarize the uses of silica, or silicon dioxide.
2. How do you account for the small seams or ridges seen along the sides of cheap bottles?
3. Glass fruit jars generally have a greenish tint. What causes the color? Is it an advantage or a disadvantage?
4. Would it be to a milk dealer's advantage to buy milk bottles that have a green tint? Explain. Try the effect.
5. How does ordinary glass differ from hard glass in its composition?
6. What are the advantages in the use of pyrex glass?
7. Why should aqua ammonia never be used for washing cut glass?

8. What is meant by "non-shatter" glass? Why is it being used extensively at the present time?
9. What is meant by water glass? For what purposes is it used?
10. How is frosted glass made? Give two methods.

## GROUP B

11. Sodium hydroxide attacks glass and roughens the surface. This effect makes it difficult to remove the stoppers from glass-stoppered bottles that contain sodium hydroxide. Will sodium carbonate solution have the same effect? Explain.

12. A student in the laboratory melted some sodium carbonate in a silica crucible. He was astonished when the bottom dropped out of the crucible. Explain what chemical action occurred.

13. Why is "resistance" glass so important for laboratory use?

14. Igneous rocks are of volcanic origin. Why is sand the final product in their disintegration?

15. Explain the steps in the manufacture of window glass. What is meant by annealing glass, and why is it important?

16. What is the composition of flint glass? What are its properties?

17. Why does plate glass make better mirrors than ordinary blown glass?

## PROBLEMS

## GROUP A

1. How many grams of sodium silicate can be made by the action of an excess of silica on 400 gm. of sodium carbonate?
2. How many pounds of hydrofluoric acid are needed to interact with 40 lb. of  $\text{SiO}_2$ ?

## GROUP B

3. How many liters of carbon dioxide at 740 mm. and  $20^\circ \text{C}$ . will be liberated by the action in Problem 1?

4. In what proportions should the sand, limestone, and sodium carbonate be mixed in making glass, assuming that the final product will be made up of equal molar quantities of sodium and calcium silicates?

## CHAPTER 29

### COLLOIDAL CONDITION OF MATTER

#### Vocabulary

**Micron.** A unit of measurement equal to 0.001 of a millimeter.

**Sol.** A colloidal suspension which resembles in appearance a true solution.

**Gel.** A colloidal suspension that appears semi-solid, or jelly-like.

**Triturate.** To rub or grind to a very fine powder.

**Humus.** Partially decomposed organic matter found in fertile soils.

**Gangue.** Earthy or rock impurities found mixed with ores.

**Enzyme.** An organic substance which acts as a catalyst in producing some types of fermentation.

**405. Introductory.** The characteristics of *true solutions*, such as the solutions of salt, sugar, etc., were studied in an earlier chapter. We also learned that such substances crystallize when the solvent is evaporated. They are known as *crystalloids*.

Such non-crystalline substances as glue and gelatine *appear* to dissolve in water, but a more careful study shows that they do not form true solutions. Starch forms a paste with hot water, but it does not really dissolve in the water. When the water that was added to glue, gelatine, or starch is expelled by evaporation, not one of them crystallizes. Substances like starch, glue, gelatine, white of egg, and jelly are known as natural *colloids*, from the Greek word *kolla*, which means "glue."

**406. Ordinary Suspensions and Colloidal Suspensions.** If we stir some fine sand with water, we form temporarily a *suspension*. When the agitation is stopped, the sand soon settles to the bottom. The finer particles settle slowly. The sand may easily be removed by filtration.

If we add a small quantity of gelatine to water, a *colloidal*

*suspension* is formed. Such a suspension does not settle upon standing. The gelatine cannot be removed by filtration. This is characteristic of the behavior of colloidal suspensions. The particles are large enough to diffuse light,

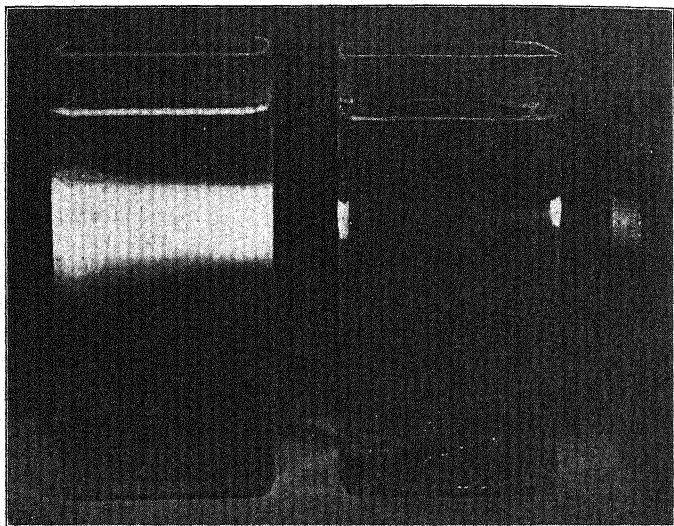


Photo by Wettlin

FIG. 239. — A beam of light is diffused by a dilute suspension of starch in the jar at the left. The jar of pure water at the right does not diffuse the light.

but they cannot be seen with a microscope. (See Fig. 239.) The following table summarizes the differences between ordinary and colloidal suspensions:

Behavior	Colloidal suspensions	Ordinary suspensions
Settles upon standing	No	Yes
Can be removed by filtration.....	No	Yes
Size of particles.....	0.1 $\mu\mu$ — 100 $\mu\mu$	1 $\mu$ — 1 mm., or more

$\mu$ , called a micron, equals 0.001 mm.

$\mu\mu$ , called a millimicron, equals 0.000,001 mm.

**407. Colloidal Suspensions and True Solutions.** There are several ways in which colloids in suspension differ from true solutions. On the other hand, there are some ways in which they resemble one another in their behavior. In 1861 Graham separated colloids from crystalloids by *dialysis*. He inclosed both colloids and crystalloids in a parchment bag which he suspended in water. (See Fig. 240.) The crystalloids passed through the parchment readily by osmosis, but the colloids were retained almost entirely. This method of separation indicates that the particles of solute are much smaller than the particles in a colloidal suspension. The colloidal particles are probably *aggregates* of molecules, or very large single molecules. In the following table, the behavior of colloidal suspensions is compared with or contrasted with that of true solutions:

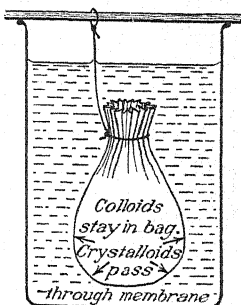


FIG. 240.— Colloids may be separated from crystalloids by dialysis.

Behavior	Colloidal suspensions	True solutions
Size of particles . . . . .	Large enough to diffuse light	Too small to diffuse light
Settles upon standing .	No; or slowly	No
Can be removed by filtration . . . . .	No	No
Can be seen by aid of microscope . . . . .	No	No
Pass through a membrane easily . . . . .	No	Yes
Lower freezing point of solvent, or medium .	Little, or none	Yes, decidedly
Raise boiling point of solvent, or medium .	Little, or none	Yes, decidedly

**408. Nature of Colloids.** According to Bancroft, "colloid chemistry is the chemistry of grains, drops, bubbles, filaments, and films." The particles may average about 0.000,001 mm. in diameter. When a colloid is *dispersed* in a liquid, it is often spoken of as a solution. Chemists call such solutions *sols*. Sometimes a hot *sol* in cooling sets and forms a jelly-like mass known as a *gel*. Glue and gelatine are common examples. When a *gel* is formed, it adsorbs a large quantity of water, but the material appears to be solid or semi-solid.

When glue that has formed a *gel* is warmed with a little water, it *reverts* to the sol phase. Such a colloid is said to be *reversible*. Gelatine, for example, forms the *gel phase* when chilled, but reverts to the *sol phase* when it is heated. Some colloids are *irreversible*. The white of egg may be converted into a gel by heating it, but it cannot be changed back into the sol phase.

As we subdivide an object, its surface area increases. If such subdivision is continued until the diameter of the particles is only about 0.000,001 mm., the increase in area is tremendous. Because the area is so great, colloids are capable of *adsorbing* on their surfaces large quantities of matter. The adsorption of gases by charcoal is an example. If an acid is added to a water-glass solution, a substance with an enormous number of capillary pores is produced. This product, which is known as "silica gel," is extensively used as a drying agent and to adsorb offensive gases. Colloids often take up the liquid in which they are suspended, and swell in size enormously. The force of such expansion is tremendous. *One of the most important properties of colloids is that of adsorption.*

Colloidal particles are electrically charged, some of them positively, and others negatively. Suppose we have given a colloidal suspension whose particles are positively charged. If we add to it a suspension that has negatively charged





gold wires used as terminals. (See Fig. 242.) A colloidal sol of finely divided gold is formed. Such a sol has a purplish color, and the particles remain suspended more or less indefinitely. Similar sols may be made by using for the terminals wires made of silver, platinum, or copper.

2. A sol may be produced by grinding or triturating the substance until it forms a fine powder. The strength of concrete seems to depend to a considerable extent upon the fineness of the cement of which it is made.

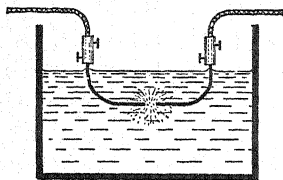


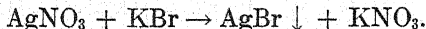
FIG. 242. — Apparatus for forming colloidal metals.

There are special mills for grinding substances for making colloids.

3. If we dissolve stannous chloride,  $\text{SnCl}_2$ , in water, some hydrolysis occurs. The stannous hydroxide that is produced forms a colloidal suspension. Many colloidal suspensions are formed in a similar manner by *hydrolysis*.

4. The formation of sols merely by adding the dispersing medium has been mentioned. Hot water added to starch in making a starch paste is a familiar example. The various lacquers are colloidal suspensions of some plastic, such as nitro-cellulose or cellulose-acetate, in such solvents as butyl alcohol or butyl acetate. Such plastics are *true colloids*.

5. If we add 10 c.c. of a molar solution of silver nitrate to 10 c.c. of a molar solution of potassium bromide, complete precipitation of the silver bromide occurs as represented by the equation,



If we add a *large excess* of silver nitrate to a solution of potassium bromide, *colloidal* silver bromide is formed. Practical use is made of this fact in making the emulsion for photographic films and plates.

**411. How Colloids Can Be Precipitated.** Since colloids

cannot be separated from the dispersing medium by filtration, they make trouble for the chemist in analytical work. We have already learned that one colloid may be precipitated by adding another whose particles are charged with electricity of opposite sign. Electricity of high voltage is used to precipitate mist and dust. If we add an acid to some sweet milk, the protein suspended in the milk is precipitated. Many colloids may be precipitated by the addition of a dilute acid. Sometimes alkalis are used for a similar purpose. In general, electrolytes precipitate colloids.

The formation of deltas by the Nile and the Mississippi Rivers, for example, is an interesting illustration of the precipitation of colloids. The particles of silt carried by rivers is precipitated when it comes into contact with the salt waters of the ocean or the sea. The precipitation of such material builds up the deltas.

**412. How the Chemist Stabilizes Colloids.** Sometimes it is important to prevent the precipitation of colloids. The blood stream and the nerve tissues are colloidal. A precipitation of either one would cause death. Dr. Fischer, of the University of Cincinnati, at one time stated that it was his opinion that the bad effect of alcohol upon the human body is due to its tendency to precipitate colloids. Undoubtedly a colloidal suspension remains permanent if the charges on the particles can be maintained, because charges of like sign repel one another. There are several substances that can be added to stabilize a colloidal suspension. Such substances are believed to stick to the colloidal particles and prevent their adhering to one another. The preparation of aquadag, a suspension of graphite in water, has been discussed. Acheson uses *tannin* to stabilize this suspension. When a pharmacist makes an emulsion, he triturates the oil and the dispersing medium with *gum arabic*, or *gum tragacanth*. Such *protective* colloids make the emulsion more stable, or more permanent. Gelatine added to milk tends to keep it

from curdling. When gelatine is added to ice cream, it prevents crystallization and makes the product much smoother. It is especially necessary to have such a protective colloid unless the ice cream is stirred constantly while it is being frozen. An emulsion of silver bromide is permanent in the presence of gelatine; this fact is utilized in making photographic films. In electroplating, it has been found that one metal does not adhere well to another if it is deposited in the form of crystals. Hence, protective colloids are added to the electrolyte in many plating baths.

**413. Kinds of Colloids.** In discussing colloids, we have referred to one type only — the dispersal of a solid in a liquid. Smoke and dust are examples of solids that are sometimes dispersed in a gaseous medium. The color in glass is caused by the dispersion of small particles of one solid in another solid. A trace of gold or selenium will color a large quantity of glass. Thus we find that it is possible to have a *solid dispersed in a liquid*, in another solid, or in a *gaseous medium*.

Milk is an example of an emulsion in which droplets of liquid are dispersed in another liquid. Many emulsions are sold as medicine. Mayonnaise dressing is also an example of an oily liquid dispersed in another liquid. The foam produced when root beer or soda water is drawn from a fountain is an excellent example of a kind of colloid where a *gas* is dispersed in a liquid medium. To summarize, we find it possible to have *solids, liquids, or gases dispersed in a liquid medium*.

A fog or a mist is really converse to the colloidal condition of foam. Here we have a *liquid dispersed in a gaseous medium*. In the use of leavening agents, we find gases dispersed in a solid medium.

**414. Why Colloids Are Important.** By this time the student must conclude that colloids are all around him, and that they are of great importance. We may refer briefly to

a large number of important applications of colloidal chemistry, and then devote more space to a few particular cases.

The adhesive properties of glue, mucilage, and varnish are due to their colloidal nature. Paint is a pigment or a white solid dispersed in an oil medium. The manufacturers of paints would pay a large price to someone who can find a perfect stabilizer for such a suspension, one that will prevent the settling of ready-mixed paints in the can. The adsorptive properties of certain dyes cause them to stick to the fibers of cloth. Hides contain a colloidal substance that is precipitated by tannin, another colloid, in the making of leather. Such chemicals as the compounds of chromium are sometimes used for the same purpose. The strength of cement and asphalt, and their ability to resist wear are said to depend upon the fineness of the particles of which they are made.

In the laundry, the kitchen, and the lavatory, soap is used to emulsify the fats and oils that hold the dirt, and to break up the dirt into fine particles. It also serves as a protective colloid to keep dirt particles dispersed in the wash water.

Some soils have all the elements needed for plant growth, and yet they are not fertile. They need humus, an organic colloid, to keep the fine particles from coalescing. Thus the soil can adsorb water which carries the mineral matter to the roots of the plants. Salt and alkalis destroy the humus and make the soil infertile.

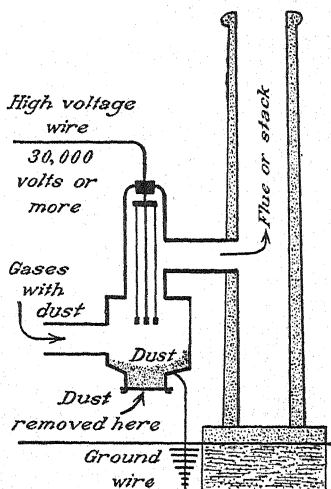


FIG. 243. — Sectional drawing to show arrangement of the parts of a Cottrell precipitator.

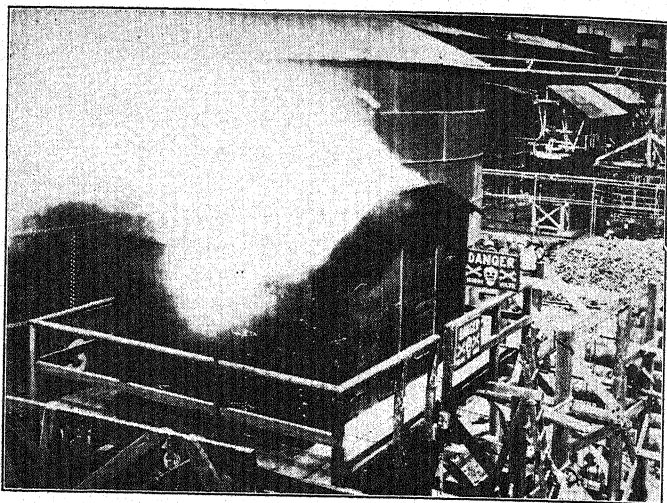


FIG. 244. — Plant fitted with Cottrell precipitator. Note mist when current is off.

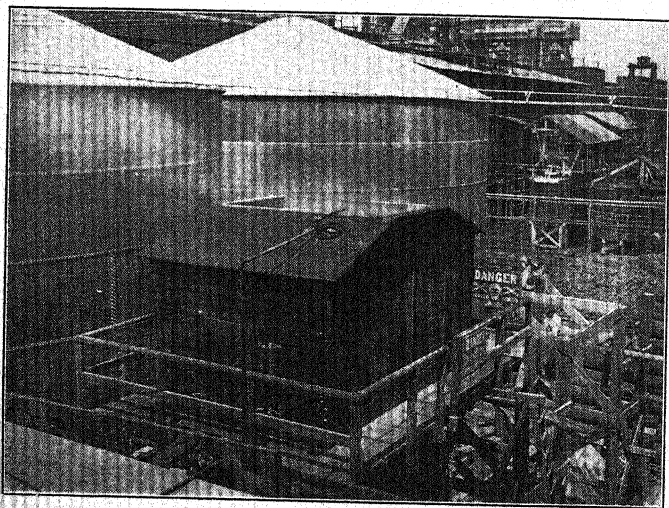


FIG. 245. — Plant fitted with Cottrell precipitator. Mist disappears when current is turned on.

If we add 15 c.c. of a concentrated solution of calcium acetate to 85 c.c. of alcohol, a jelly-like substance is formed. This product is called *solid alcohol*. It is used as "canned heat." Stearic acid in alcohol produces a similar result.

In making jellies, pectin is used with the fruit juice. Some fruits contain sufficient pectin to cause fruit juices to form a colloidal gel, but some are so deficient that pectin must be added to the juice.

#### 415. How Cottrell Solved the Dust and Mist Problem.

The smelters in certain localities at one time belched out from their stacks tons of dust. Such dust was a nuisance, causing discomfort to those in the vicinity, and in some cases poisoning animals that grazed upon the dust-covered vegetation. Some of the dust contains valuable chemicals, such as the oxides of arsenic and other metals. Around sulfuric acid plants, too, acid mists are decidedly annoying.

Cottrell, an American chemist, devised a method of precipitating acid mist and dust particles. He uses electricity of high voltage; sometimes as high as 75,000 volts are used. Metal plates are attached to the inner walls of smelter stacks, and wires are so suspended that they dangle in the center of the flue or stack. When the current is turned on, the dust particles become charged with electricity of the same sign as that on the suspended wires. They are repelled by the wires and attracted to the metal plates upon the walls. (See Fig. 243.) Then the material is recovered after precipitation. Acid mist is precipitated in a similar manner. Figure 244 shows a plant surrounded by mist. Figure 245 shows how the mist disappears when the current is turned on for a *Cottrell precipitator*.

**416. How Firefoam Extinguishes Fires.** Water thrown on a fire from burning oils, lacquers, or other light flammable liquids sinks to the bottom of the container, and the fire continues to burn. (See left-hand side of Fig. 246.) The carbon dioxide extinguisher shown in Fig. 154 is no more effec-



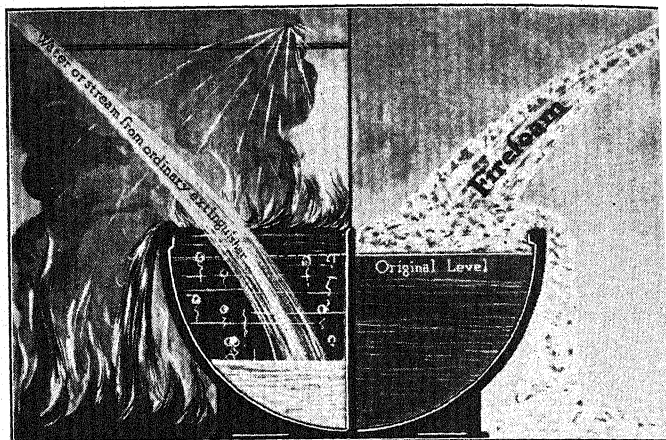
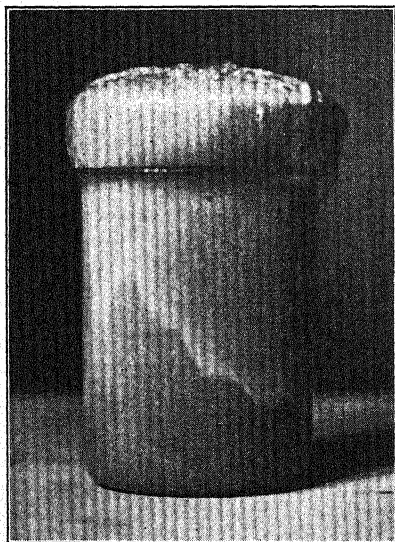


FIG. 246. — Diagram to illustrate the principle of smothering fires by the use of foam.



*Photo by Wettlin*

FIG. 247. — Two hundred c.c. of solution fill a liter beaker with foam. A little licorice extract is used to make a tough foam.



tive, because the carbon dioxide escapes too rapidly. By the use of a colloid to retain the carbon dioxide and form a foam or froth, such fires can be smothered. (See Fig. 247.)

In the firefoam type of extinguisher sodium bi-carbonate is used to supply the carbon dioxide, and a solution of alum or aluminum sulfate is used to interact with the bi-carbonate and set free the carbon dioxide. An extract of licorice, or some other colloid, is used to prevent the escape of the gas and to form a blanket of foam. Such a blanket, which may be several inches thick, shuts off the oxygen supply and smothers the fire. (See right-hand side of Fig. 246.)

Automobile parts and many other articles are now lacquered by immersing them in dipping tanks. The fluid is highly flammable. Such tanks are often fitted with firefoam extinguishers which operate automatically when a fire starts. Figures 248 to 251 show how foam is used to extinguish a fire in a tank of burning oil.

**417. How Colloidal Foam is Used to Concentrate Ores.** Very few ores are found pure in nature, but they are generally mixed with some earthy material, known as *gangue*. Before the metal can be extracted profitably, it is necessary to get rid of some of the impurities mixed with the ore, or to *concentrate* the ore. In the case of copper sulfide, for example, it is interesting to find that oil wets, or adheres, to the copper sulfide more readily than it does to the earthy impurities in the copper sulfide ore. On the other hand, water adheres to the earthy impurities more readily than it does to the copper sulfide. The impure ore is powdered and stirred into a tank of water to which a little oil is added. The oil adheres to the copper sulfide. Air is bubbled up through the liquids in the tank. Air bubbles are adsorbed by the film of oil on the surface of the ore. In fact enough air is adsorbed to float the ore, which may be several times as dense as water, to the surface of the tank where it is removed. The gangue, which is lighter than the ore, but heavier than water, sinks

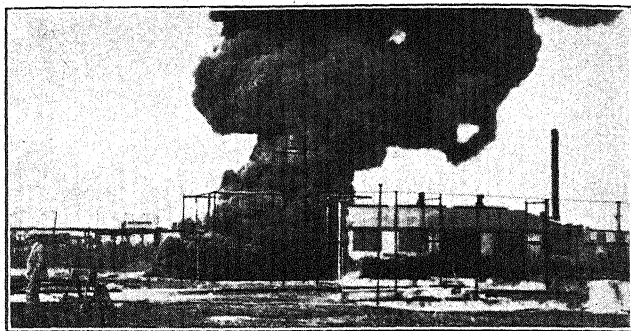


FIG. 248. — Fire from burning oil.

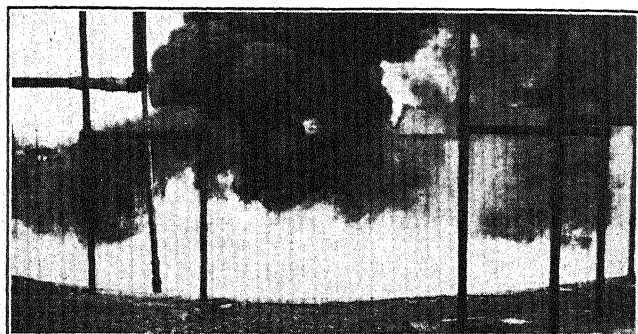
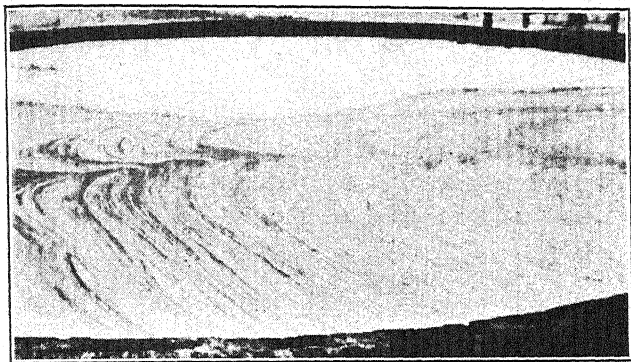


FIG. 249. — One second after foam is applied.



FIG. 250. — Fire extinguished completely as foam covers tank.



*Courtesy of Pyrene Mfg. Co.*

FIG. 251. — A close-up view which shows how the tough foam excludes the oxygen.

to the bottom of the tank. (See Fig. 252.) Thus the ore is separated from the gangue. It is estimated that 60,000,000 tons of copper ore are concentrated annually by this process.

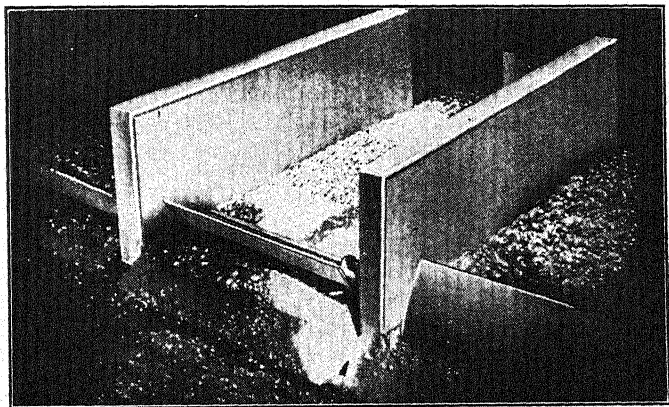


FIG. 252. — Froth-flotation tank for concentrating ores.

Other ores are concentrated by the *froth-flotation process*.

**418. How Colloids Are Related to Life.** When a seed falls into the ground, it adsorbs water, and swells decidedly.

The starch, a natural colloid which was stored in the seed, is changed by enzymes into sugar which dissolves, and can be readily transported to different parts of the seedling as growth occurs. The leaves of the plant then manufacture more starch from carbon dioxide and water. This starch may be stored as a future food supply, or it may be converted into cellulose or protein.

In the animal body, starch, proteins, and most emulsions cannot be absorbed into the body directly. They must be changed by enzymes, or ferments, which are really catalysts used in the digestive process, into smaller particles that can be absorbed more rapidly. Then in some mysterious manner protoplasm is formed. From the blood stream which carries food material in a colloidal state, the various cells in the body select the particular kind of food that is needed for their development. With few exceptions, the cells are composed largely of colloidal protoplasm. The blood, the nerve tissues, and the muscle cells are examples of colloids in the animal body. When a cell is pricked or injured, it adsorbs water and swelling results. When a bee stings one, it introduces a small quantity of acid which disturbs the colloidal condition and causes swelling.

### SUMMARY

The material in ordinary suspensions settles upon standing; the colloid does not settle when a colloidal suspension stands. Matter may be filtered out of an ordinary suspension, but colloids cannot be separated from the dispersing medium by filtration.

Colloidal particles are large enough to diffuse light; solute particles are not. The former can be detected by the aid of the ultramicroscope. Colloidal suspensions have little effect upon the freezing point and boiling point of the liquid in which they are dispersed. They do not pass through a membrane easily by osmosis. The solute in a true solution lowers the freezing point

of the solvent and raises its boiling point. It passes through membranes by osmosis.

In such *natural colloids* as glue, gelatine, and starch, the particles are believed to be large molecules. Some substances that are not naturally colloidal may be dispersed by the *electric arc*, by *fine grinding*, by *hydrolysis*, or by the use of a *large excess* of one reagent during metathesis.

Colloids may exist in the *sol* phase or the *gel* phase. Some are reversible. *Adsorption* is one of the marked characteristics of colloidal suspensions.

One colloid may be precipitated by adding to it another whose particles are charged with electricity of opposite sign. Electrolytes are often used to precipitate colloids. Heat coagulates some colloids.

Some colloids protect others and retard or prevent their precipitation.

It is possible to have solids dispersed in other solids, in liquids, or in gases; liquids may be dispersed in other liquids or in gases; gases may be dispersed in liquids, or in solids.

Colloidal chemistry is of interest to many manufacturers. It plays a part in such industries as those of making rubber, varnish, paint, celluloid, asphalt, cement, and leather. Protoplasm as found in nature is colloidal.

The *Cottrell process* is used to precipitate dust, smoke, and mist by means of electricity. *Firefoam* is a gas dispersed in a liquid that finds use in extinguishing oil fires. The *froth-flotation process* is used to separate some ores from their impurities.

## QUESTIONS

### GROUP A

1. How would you test a liquid to determine whether it is a true solution or a sol?
2. Of what advantage would a protective colloid be to a manufacturer of ready-mixed paints?
3. Why is the study of colloids of such great practical importance?
4. Nitric acid causes white of egg to coagulate. Explain.

5. Does alcohol coagulate protein? What effect would you expect strong alcohol to have upon the nervous system?

6. What is the Cottrell process? In what industries is it used?

7. For what types of fires is firefoam especially suitable? Explain how it extinguishes a fire.

8. How does boneblack decolorize sugar?

9. Explain the difference between the terms "absorption" and "adsorption."

10. How would you proceed to separate sugar from gelatine in water solution?

11. Contrast the properties of a true solution with those of a colloidal suspension.

12. What are the differences between an ordinary suspension and a colloidal suspension?

13. How is soap useful as a cleansing agent?

#### GROUP B

14. Does gelatine in ice cream make it more easily digestible? Explain.

15. Gelatine is sometimes added to cow's milk that is to be given to infants. Why?

16. Why does the sting of a bee or the bite of an insect cause swelling?

17. Explain the effect of churning or whipping cream for a long time.

18. In the froth-flotation process, explain why the dense ores float and the lighter impurities sink.

19. Upon what properties do the uses of "silica gel" and "activated charcoal" depend?

20. India ink contains finely divided particles of carbon suspended in a liquid that contains some gum arabic. What is the purpose of the gum arabic?

21. What does the term "Brownian movement" mean? What is its cause?

22. Explain why nearly all the recipes for "frozen desserts" to be made in household refrigerators include gelatine.

## CHAPTER 30

# OCCURRENCE AND EXTRACTION OF METALS

### Vocabulary

**Sinter.** To form a coherent mass or clinker by heating loose material with some tarry material as a binder.

**Autogenous.** A type of welding where two pieces of metal are united by fusing or melting them together.

**Flux.** A substance used in metallurgy to lower the melting point or to make the mineral or metal more fluid.

**Tuyère.** A nozzle through which an air blast is delivered.

### A. OCCURRENCE OF METALS

**419. Introductory.** We have studied the most important of the non-metals, or the acid-formers. With the exception of boron, the elements that remain to be studied are metals, usually base-formers. It is of interest to inquire how such elements occur in nature. There are six or seven ores of copper, five or six of iron, and five or six of zinc. To study each ore would involve a great deal of pure memory work. Hence, an attempt is made in this chapter to so outline the general characteristics of metals and their compounds that it will be possible for the student to get a general idea of the occurrence of metals without too much detail. Such a plan depends upon a careful study of the *activity* of the metals, and of the *stability* and *insolubility* of their compounds.

**420. Metals Occurring Free.** In Chapter 5 we learned that some metals are extremely active, and others very inactive. We would hardly expect to find such an active metal as sodium occurring uncombined in nature. It would



## 492 OCCURRENCE AND EXTRACTION OF METALS

interact with the oxygen or the carbon dioxide present in the air, or with water. But platinum and gold are inactive; they do not combine readily with other elements. *Such metals occur free or uncombined in nature.* Other metals that occur free in nature are copper and silver.

**421. Metals That Occur As Oxides.** Oxygen is such an active non-metal, and it is found so abundantly that we would expect to find many oxides of metals occurring in nature. Such is the case. The most important ores of iron, tin, aluminum, and manganese are oxides. The oxides of copper and zinc are also found to some extent. These oxides are all *insoluble* in water, and they are *stable* compounds. On the other hand, we *would not expect* to find soluble oxides, or those which unite chemically with water. In fact, any oxides of sodium, potassium, calcium, or barium that are exposed to atmospheric conditions soon unite with water to form hydroxides, or with carbon dioxide to form carbonates.

**422. Metals That Occur As Sulfides.** Like oxygen, sulfur is widely distributed in nature, and it is active. The sulfides of such heavy metals as iron, copper, zinc, lead, tin, silver, nickel, and mercury are found in nature. Some of them are the most important ores of the metals. Such sulfides are *insoluble* and they are *stable*. The sulfides of such light metals as sodium, potassium, calcium, and barium hydrolyze in water. They are not found in nature.

**423. Metallic Hydroxides in Nature.** The hydroxides of sodium, potassium, calcium, and barium are all soluble in water. They are not found in nature. The hydroxides of the heavy metals named in the preceding section are all *insoluble*, but they do not occur in nature because they are not very stable. They are likely to lose water and form the oxide, or to combine with hydrogen sulfide to form an insoluble sulfide, or to unite with carbon dioxide to form a carbonate. The *hydrated oxides* of aluminum and iron are found in nature, and some *basic carbonates* occur abundantly.

A *basic salt* is one in which not all of the hydroxyl ions of the base have been replaced by negative ions of an acid.

**424. Carbonates in Nature.** The carbonates of sodium and potassium are *soluble* in water. They are not found in nature. Other carbonates are insoluble. The carbonates as a group are fairly stable, and carbon dioxide occurs in the air and also dissolved in natural waters. For these reasons, we would expect to find carbonates in nature. The carbonate of calcium is widely distributed, and it occurs abundantly. Other carbonates found in nature include those of barium, strontium, zinc, iron, copper, and manganese.

**425. Silicates in Nature.** In Section 399 we learned that all silicates are insoluble except those of sodium and potassium. Many silicates are found abundantly in nature. As a rule they do not make satisfactory ores, because *mixed* silicates are so common. It is difficult to extract the metals from *complex* silicates and to separate them from one another, if the operating costs are to be kept low.

**426. Metals That Occur As Sulfates.** Nearly all the compounds just mentioned are insoluble. The *sulfates*, however, are *generally soluble*. The sulfates of barium and lead are *insoluble*; those of calcium and silver are *slightly soluble*. Just as we might expect, the insoluble sulfates of lead, calcium, and barium are found in nature. The soluble sulfates do not occur extensively in nature, although some sulfates of sodium, potassium, and magnesium are found in certain localities.

**427. Metals That Occur As Chlorides.** The only insoluble chlorides are those of lead, silver, and mercurous mercury. Contrary to what one might expect, there are several soluble chlorides that are found in nature. They are found in sea water, or in deposits left by the evaporation of the water from some land-locked parts of prehistoric seas. The chlorides found include those of sodium, potassium, and magnesium. Since all the compounds of sodium and potas-

sium are soluble, it is not so strange after all to find these metals in nature in such stable compounds as the chlorides.

**428. Metallic Nitrates.** *All nitrates are soluble.* Sodium nitrate is found in the desert regions of northern Chile. It is the only nitrate that occurs in nature to any considerable extent.

## B. METALLURGY

**429. What Is Meant by Metallurgy?** That science which deals with the methods of extracting metals from their ores is called *metallurgy*. In discussing the methods used, we shall have occasion to refer to both *minerals* and *ores*. All ores are minerals, but not all minerals are used as ores. The term *mineral* refers to any element or compound that occurs naturally in the earth's crust. Clay is a mineral that contains aluminum, but it is not an ore of aluminum because it is impossible to extract aluminum from clay at a profit. *An ore is a mineral that contains an element in such quantity and in such a form that it may be profitably extracted.* Bauxite is an aluminum mineral from which the aluminum can be extracted profitably. Hence bauxite is an ore of aluminum, as well as an aluminum mineral.

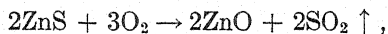
In this chapter we shall aim to describe in some detail and illustrate certain general methods of extracting metals from their ores. These processes are typical of those used in extracting several other metals. For example, aluminum is extracted by means of electrolysis. The process described for extracting aluminum is typical of that used for extracting other elements, such as sodium, potassium, or magnesium. Iron is extracted from its ores by reducing them with carbon in the form of coke. The process, which is described in this chapter, is typical of the extraction of copper, zinc, and tin. An active metal, such as sodium or aluminum, may be used to take oxygen from a less active metal.

**430. Preliminary Treatment of Ores.** Some ores must

undergo a preliminary treatment before they can be extracted. The froth-flotation process is used to concentrate some low-grade ores. This is usually done at or near the mines. Then the bulk of material that must be shipped to the smelter is decidedly reduced, thus saving labor and freight.

Sometimes the ore is so loose and powdery that much of it would be lost during its reduction by the blast of air that is blown through it. To prevent such loss, a little tarry material is added, and a flame is directed over the surface of the material. Such cementing of dust particles to form a coherent mass is known as *sintering*.

Ores that occur as *sulfides*, *hydrated oxides*, or *carbonates* are nearly always converted into oxides before they are smelted. This is accomplished by *roasting* the ores in the open air. Such roasting drives off the water from the hydrated oxides; it also drives off the carbon dioxide and leaves the oxides of the metal. The following equation,

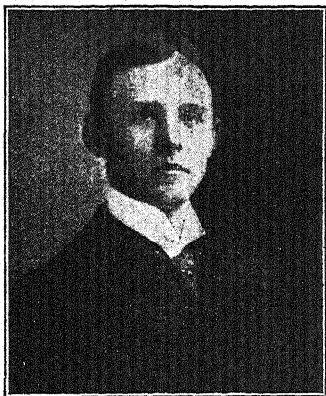


is typical of the behavior of sulfides when they are roasted in air. Thus we find that the metallurgist usually converts the ores into oxides before the metals are extracted.

### C. ELECTROLYSIS

**431. How Electrolysis Is Used.** We have already had ample proof that the electric current will decompose compounds, or separate the ions of compounds that are dissociated. The ionization must precede such separation. The ore used as the electrolyte must be some soluble compound, or it must be melted or fused in order to ionize it. But few natural ores are soluble; therefore the ore is generally *melted* or *fused*. For example, in preparing sodium, the electric current is passed through *melted* sodium hydroxide.

The sodium hydroxide used is soluble, but when the electric current is passed through a solution of sodium hydroxide, the



*Permission of Popular Science Monthly*

Charles Martin Hall (1863-1914) was an American inventor. He was awarded the Perkin medal in 1911.

sodium that is set free immediately attacks the water that is present, and forms sodium hydroxide. Such metals as sodium, potassium, calcium, magnesium, and aluminum are extracted by means of the electric current.

In the United States, electrical industries flourish at Niagara Falls, where use is made of the hydro-electric power that is developed. The most widely used metal that is extracted by electrolysis is aluminum.

**432. How Aluminum Is Extracted.** In the chemical laboratory of Oberlin College, Professor Jewett made the following remark: "Any person who discovers a process by which aluminum can be made on a commercial scale will bless humanity and make a fortune for himself." As he left the laboratory, a student, Charles Martin Hall, remarked to a classmate, "I'm going for that metal." Two years later Hall handed Professor Jewett a lump of aluminum that he had extracted by the following process:

Bauxite, a hydrated oxide of aluminum, is first roasted to drive off the water. But aluminum oxide is insoluble in ordinary reagents, and it fuses at about  $2000^{\circ}\text{C}$ ., well above the melting point of iron. Hall's problem was to find a solvent in which the aluminum oxide will ionize. He discovered the fact that cryolite, a double fluoride of sodium and aluminum that is found in Greenland, not only melts at a low temperature, but it also dissolves bauxite, or alu-

minum oxide. This discovery proved to be the key to his problem.

An iron box lined with carbon is made the cathode, and rows of carbon rods are used as anodes. (See Fig. 253.) The box is kept at a temperature higher than the melting point of cryolite. When the current is passed through the solution, the aluminum ion is attracted to the cathode where its charge is neutralized. Molten aluminum collects at the

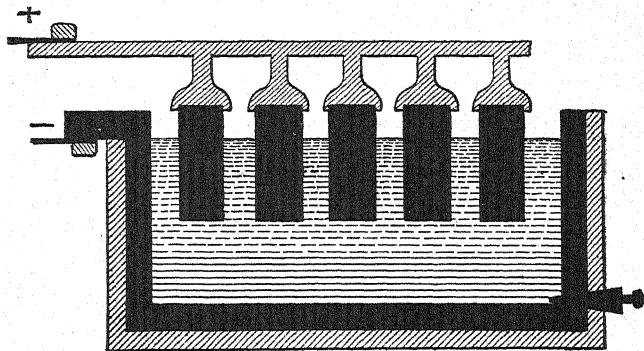


FIG. 253. — Electrolysis of aluminum oxide.

bottom of the tank, where it is drawn off periodically. The oxygen ion is attracted to the anode where it loses its electric charge. Oxygen gas escapes at the anode, or combines with the carbon of the anodes. Aluminum oxide is added from time to time to keep the action continuous. It is interesting to note that Heroult, working independently in France, also worked out a commercial process of extracting aluminum by electrolysis at about the same time that Hall succeeded here in America.

Aluminum was first isolated in 1828 by Wöhler, a German chemist, under whom Professor Jewett studied. In 1855 aluminum sold at \$90 per pound. The price in 1870 was \$12 per pound. In 1886, Hamilton Castner, of Brooklyn, learned how to make sodium cheaply enough so it could be used to

take oxygen from aluminum. Castner's process reduced the price of aluminum to less than \$2 per pound. The Hall process, which was commercialized in 1889, is so successful that the market price for aluminum is now about 20¢ per pound. The numerous uses to which aluminum is put must convince us that Hall conferred a blessing upon mankind. When Hall died in 1914, he left a bequest of several million dollars (a part of the wealth he had acquired as a result of his discovery) to Oberlin College.

#### D. REDUCTION WITH CARBON

**433. Reduction.** The reduction of the oxides of metals with carbon is the most important method employed in metallurgy. The reducing agent generally used is *coke*, since it is efficient and not very expensive. Charcoal was employed at one time, and coal is sometimes used. Every year the United States produces about 40,000,000 tons of iron. When we consider that approximately 1 lb. of coke is needed to make 1 lb. of iron, we can understand why some 100,000,000 tons of soft coal are converted into coke every year. Furthermore, iron is only one of the metals extracted by this method. Copper, tin, and zinc are obtained by reduction. Let us study somewhat in detail the operation of a blast furnace in the preparation of iron as typical of this general method of extracting the useful metals.

**434. How Iron Is Extracted by the Use of a Blast Furnace.** 1. *The furnace* itself is one of the giants used in industry. It consists of a steel shell from 80 to 100 ft. high, and from 20 to 25 ft. internal diameter. If the ceilings of your schoolroom are 14 ft. high, that means that the blast furnace is as tall as a school building six or seven stories high. The steel shell is lined with fire-brick. (See Fig. 254.) Water circulates through a shell built into the walls in order to protect those portions of the furnace that are subjected to the



greatest heat. The heat is due to the chemical reactions that take place inside the furnace. The action is started by forcing a blast of hot air into the furnace through tuyères. Hence the name *blast furnace*. Figure 255 shows a blast fur-

nace with the "stoves" that are used for heating the air blast. These "stoves" are almost as large as the furnace itself. They are filled with a checker-work of brick which is heated with gas. Then air is heated by being blown through the checker-work of heated brick. Each furnace has several "stoves."

2. *The charge* consists of iron ore in the form of *iron oxide*, of *coke*, and of a *flux*. The charge generally consists of about 3 parts by weight of ore, 2 parts of coke, and 1 part of limestone. The limestone is used as a flux when the ore contains silica as an impurity. When the gangue in the ore is limestone, then silica is used as a flux. Some of the largest blast furnaces use about 2000 tons of raw material every 24 hours.

3. *The operation.* While some of the "stoves" are being heated by the use of blast furnace gas, others are being used to heat the air blast. Huge blowers are used to force air up through the *pre-heated* "stoves." The air absorbs heat from

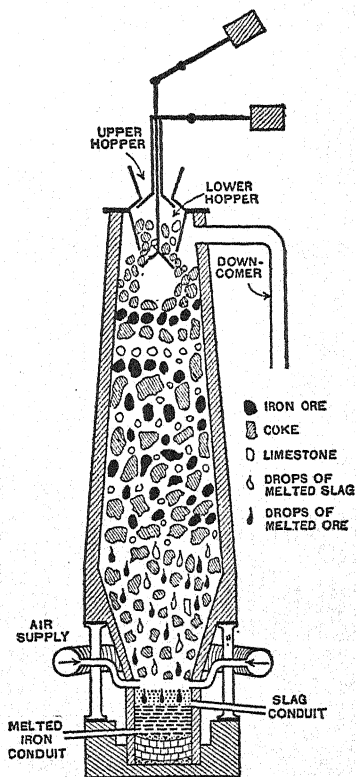


FIG. 254. — Diagram of blast furnace.

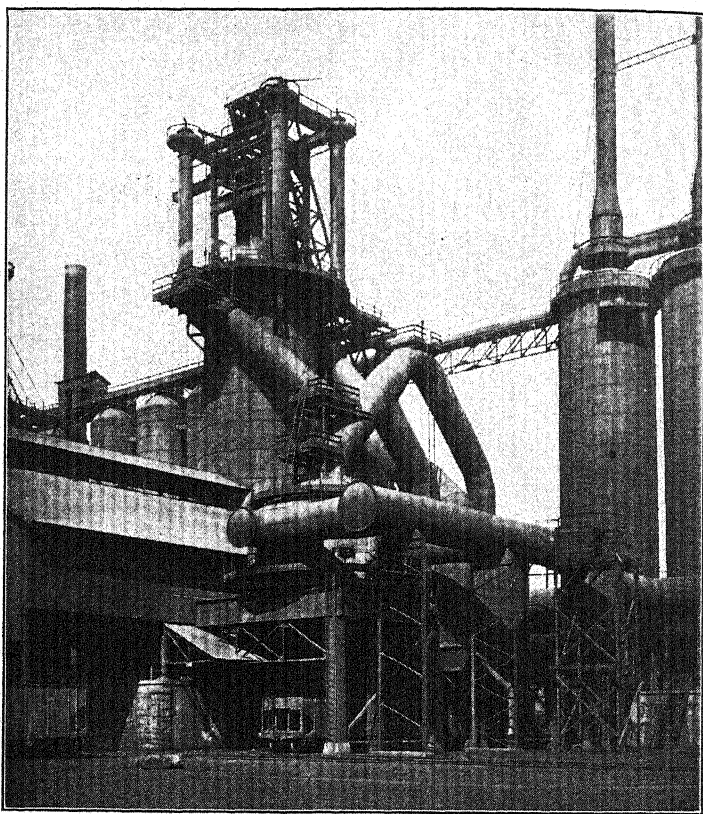
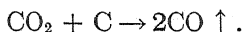


FIG. 255. — A blast furnace for reducing iron ores. The "stoves" seen at either side heat the air for the blast.

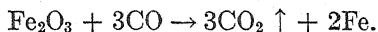
the hot brick, and the hot-air blast then enters the furnace through the tuyères. Over 50,000 cu. ft. of air, at a temperature of from 500° to 800° C., enter a large blast furnace every minute. It takes 4 or 5 tons of air to make 1 ton of iron.

4. *The action inside.* The chemical action inside a blast furnace is complex. The coke is ignited by the hot air blast and some of it burns to carbon dioxide. But as the carbon

dioxide that is formed just above the tuyères rises it comes into contact with more coke and it is reduced to carbon monoxide.

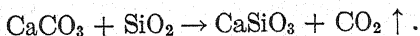


Carbon monoxide is a good reducing agent and it reduces the iron oxide to metallic iron. The equation follows:



To prevent any possibility of a reversal of the reaction, the operation is so controlled that there will be a decided excess of carbon monoxide. For that reason the waste gases removed from the top of the furnace contain from 20% to 30% of carbon monoxide, a valuable fuel. This *blast furnace gas* used to be wasted. Now it is collected and it supplies enough fuel to operate the entire plant. It heats the "stoves," and supplies heat energy for power purposes. The white-hot liquid iron sinks to the bottom of the furnace where it is tapped off every 4 or 5 hours. It may be cooled in molds to form pig iron, or it may go directly to a furnace or a converter to be made into steel.

5. *The flux* serves three purposes: (a) It unites chemically with the gangue present in the ore, and forms a slag. The slag is drawn off from the furnace every couple of hours. The following equation shows the chemical action that occurs during the forming of the slag:



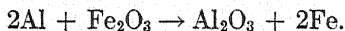
(b) *The glassy slag* (see Section 402) that is formed has a lower melting point than the impurities in the ore. Hence less heat is required when a flux is used. The word *flux* comes from the Latin word *fluere*, "to flow," and it is used in chemistry to designate any substance used to lower the melting point of a mixture to which it is added, and thus make it more fluid.

(c) *The slag* is lighter than the molten iron and floats on its surface. Here it protects the iron already reduced from being re-oxidized by coming into contact with the air that is constantly coming in through the tuyères.

A blast furnace is difficult to start, and when started it is kept in continual operation until it is worn out. A double trap is so arranged at the top that the raw materials may be added without disturbing the operation. The trap prevents the loss of gas. Some furnaces last for 20 years. The large ones make from 500 to 900 tons of iron a day.

### E. ALUMINO-THERMICS

**435. Introductory.** A very active metal may be used to take the oxygen from a less active metal. From Table 8, in the Appendix, we see that 393 large calories of heat are set free during the formation of one mole of aluminum oxide. For example, granular aluminum will take the oxygen from iron oxide if the temperature is raised to a high enough degree to start the reaction.



**436. Alumino-thermics.** While the use of aluminum to reduce other metals is too costly for general use, yet it is of practical value under certain conditions. (1) It is often used when a small quantity of *carbon-free* metal is needed. Chromium, which is used for making special steels, is sometimes extracted by this method. Manganese is another metal that is extracted by the use of aluminum. Other metals sometimes reduced by this process include uranium, titanium, molybdenum, and tungsten. (2) Alumino-thermics is sometimes used when the element is too active to be easily reduced with carbon. Silicon and boron are non-metals that are sometimes de-oxidized by the use of granular aluminum.

**437. Thermit Welding.** While aluminum is too costly

to be used for reducing iron oxide, yet the process is used to produce iron for welding purposes. The following method of *autogenous* welding was devised by Dr. Hans Goldschmidt. A mixture of granular aluminum and iron oxide, known as *thermit*, is placed in a crucible above the metals to be welded.

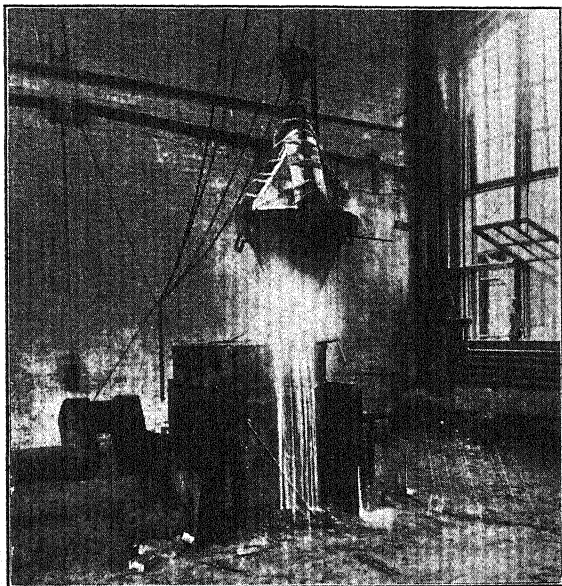
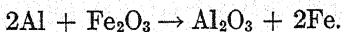


FIG. 256. — Thermit crucible as used for welding.

An igniting mixture, consisting of barium peroxide and powdered aluminum or magnesium, is placed on top of the thermit to start the reaction. (See Fig. 256.) The chemical action is as follows:



As the white hot molten iron is reduced it runs down over the broken ends and literally fuses them together to form a

solid piece. (See Fig. 257.) One of the chief advantages in thermit welding arises from the fact that the weld can be made without removing the broken parts and taking them to a large forge. Much time is saved in this way. *Black* thermit is a mixture of black oxide of iron,  $\text{Fe}_3\text{O}_4$ , and granular aluminum. The temperature produced by the reaction is estimated at about  $3500^\circ\text{C}$ . It is interesting to note that

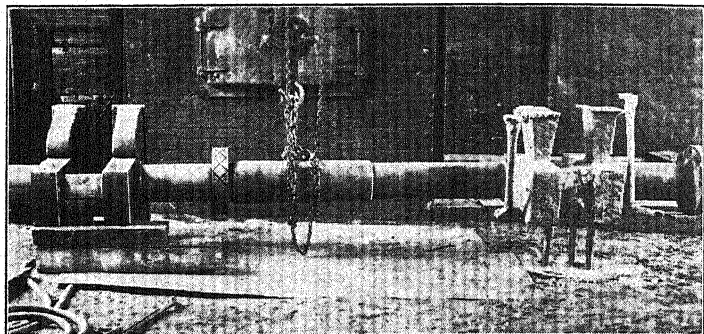
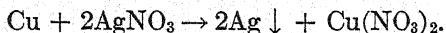


FIG. 257. — The completed weld made by the use of thermit as in Fig. 256.

thermit bombs were made during the World War and used for incendiary purposes.

#### F. METAL REPLACEMENT

**438. One Metal May Replace Another.** In Section 53 we learned that one metal will replace another from its compounds in solution. If we suspend a strip of copper in a solution of silver nitrate, the copper gradually goes into solution, and the silver is precipitated.



Use may be made of this fact in precipitating silver from its solutions by the use of a cheaper metal, such as copper or iron. Scrap iron is used to precipitate copper from the waste waters in the copper industry.

**439. Applications of the Replacement Table.** There are several interesting facts concerning metal replacement. Active metals replace those that are less active, and this fact is sometimes used to extract expensive, inactive metals from their compounds by the use of cheap, active ones.

The activity of metals is due to the readiness with which they ionize; or we may say that a metal is active if it loses its electrons easily. Potassium shows a greater tendency to ionize than any metal in the replacement series. (See page 76.) Hence it stands first in the series. The fact that potassium loses its electrons so easily makes it useful for coating the inside of the photo-electric cell used in television. (See Fig. 258.) Light shining upon it causes it to emit electrons.

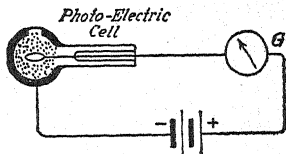


FIG. 258.—Photo-electric cell.

The farther apart any two elements stand in the series, the greater the voltage produced when those two elements are used to make a voltaic cell. For that reason this series is sometimes called an *electromotive series*. If we make a voltaic cell out of copper and zinc, the copper will be positive with respect to the zinc, and it will yield an electromotive force of 1.1 volts. If silver is made the positive element, and aluminum the negative, we may have an electromotive force of more than 2 volts. Zinc is used as the negative element in nearly all types of voltaic cells, because it is the most active metal that it is practical to use. Potassium, sodium, and some of the others would attack water even when the cell was not in use. Platinum and gold are better positive elements than copper, but they are too expensive. Carbon rods are extensively used.

The replacement table shows the student that such acids as hydrochloric do not attack the metals that stand below hydrogen, and that with few exceptions it attacks readily



those that stand above hydrogen. Elements that stand above hydrogen are not found free in nature, but many of those that stand below hydrogen occur free in nature. Those that stand above manganese are prepared by electrolysis. The metals that fall below copper in the series do not tarnish in air. The oxides of some inactive metals are decomposed by heating. The majority of those metals that stand above hydrogen in the series interact with water or carbon dioxide. They *rust* or *tarnish* in moist air.

### SUMMARY

All *oxides*, *hydroxides*, and *sulfides* of metals are insoluble in water except those of sodium, potassium, calcium, and barium. In general, the oxides and sulfides of these metals interact with water and form hydroxides. The oxides, sulfides, and hydroxides of the heavy metals form some of the important ores.

All ordinary *carbonates* are insoluble except the carbonates of sodium and potassium. Many ores occur in nature as carbonates.

The *sulfates* of barium, strontium, and lead are insoluble; the sulfates of silver and calcium are slightly soluble; all other sulfates are soluble. The sulfates are not so abundant in nature as oxides and sulfides.

The *chlorides* of lead, silver, and mercurous mercury are insoluble; other chlorides are soluble. The chlorides of sodium, potassium, and magnesium are found in nature.

All nitrates are soluble. Sodium nitrate is the only nitrate found in nature in any considerable quantity.

In general we may expect to find in nature: (1) *Inactive metals occurring uncombined*. (2) *Insoluble compounds* of the heavy metals (Berthollet's law of insolubility). (3) The soluble compounds of the *active* metals, if such compounds are *stable*.

*Metallurgy* is the science that deals with the extraction of metals from their ores.

With few exceptions metals are extracted by one of the following methods: *electrolysis*; *reduction with carbon*; *reduction with some more active metal such as aluminum*; and *replacement of the*

*metal by a more active one.* Many of the light metals are extracted by electrolysis. The common heavy metals are usually extracted by reduction of their ores with carbon. Metals less widely used and the more valuable metals are extracted by alumino-thermy, or by replacement with a cheaper metal.

## QUESTIONS

## GROUP A

1. The only soluble silicates are those of sodium and potassium. Would you expect to find silicates widely distributed in nature?

2. Why are the metals that stand above hydrogen in the replacement series not found free in nature?

3. Which metal do you think would be more easily reduced, iron or copper? Iron or aluminum?

4. Distinguish between the terms: metal, mineral, and ore.

5. What is the chief objection to the use of alumino-thermics in metallurgy?

6. What is meant by the term "flux" as used in metallurgy? State its uses in extracting iron from its oxides.

7. How are Berthollet's laws related to the occurrence of metals in nature?

8. If a steamship broke a propeller shaft, why would thermit be a satisfactory material to be used for making repairs?

9. Write equations to show how zinc can be used to replace lead, tin, copper, silver, and mercurous mercury from the nitrates of the metals.

## GROUP B

10. From the position of mercury in the replacement series, what do you think would be the effect of heating cinnabar, or mercuric sulfide?

11. Why is it necessary to fuse certain ores before electrolysis can take place?

12. State the advantages and the disadvantages of extracting metals by electrolysis.

## 508 OCCURRENCE AND EXTRACTION OF METALS

13. Summarize the facts that may be learned by a careful study of the replacement series of metals.

14. What is meant by a basic salt? Compare basic salts with acid salts.

15. The iron ore from the mines in northern Michigan and Minnesota is shipped to such cities as Gary, Chicago, Detroit, and Cleveland to be smelted. Explain why the iron ore is shipped to the coal regions instead of shipping the coal or coke to the locality where the ore is found.

16. Write equations to show how aluminum can be used to replace from their nitrates the metals listed in No. 9.

### PROBLEMS

#### GROUP A

1. How many pounds of zinc oxide can be obtained from 1 ton of zinc sulfide ore, if the ore contains 5% of gangue?

2. What weight of aluminum will be needed to extract all the oxygen from 400 pounds of ferric oxide,  $\text{Fe}_2\text{O}_3$ ? How many pounds of iron will be set free?

#### GROUP B

3. How many liters of oxygen are needed for roasting 1000 gm. of zinc sulfide? How many liters of sulfur dioxide are set free?

4. How many liters of carbon monoxide are needed to reduce 500 gm. of ferric oxide? How many liters of carbon dioxide are formed?

The metal finds some use as a reducing agent. As a catalyst, it converts *isoprene*,  $C_5H_8$ , into artificial rubber. Some of the compounds of sodium are the most important known to chemistry.

**442. Sodium Chloride,  $NaCl$ .** This compound occurs in nature in sea water, in salt-wells, and in rock deposits. Rock salt is mined in some localities, but most of the sodium chloride of commerce is obtained by the evaporation of



FIG. 261. — Harvesting salt from San Francisco Bay.

natural brines, either by the use of natural or artificial heat. In the United States more than 30,000,000 barrels of salt are produced annually. New York, Michigan, Ohio, Utah, Kansas, and a few other states are large salt producers. (See Fig. 261.) Sodium chloride crystallizes in cubes. The pure salt is not deliquescent, but magnesium chloride, a very deliquescent compound, is usually present with sodium chloride as an impurity. This accounts for the fact that salt becomes wet and "packs" in moist weather.

Sodium chloride, which is the cheapest compound of sodium, is used as a starting point in the manufacture of all

sodium compounds, and also of all compounds that contain chlorine. Thousands of tons of salt are used every year as a preservative in the packing and curing of meats. Mixed with snow or ice, salt forms a good freezing mixture. It is estimated that the average American uses about eleven pounds of salt a year in seasoning his food. Considerable quantities are fed to sheep and cattle. The chart, Fig. 262, shows the important part that salt plays in the industries.

**443. Sodium Nitrate,  $\text{NaNO}_3$ .** We have already learned that extensive beds of sodium nitrate are found in the arid regions of western South America, especially in northern Chile. It is a colorless, crystalline compound, slightly hygroscopic. Large quantities of sodium nitrate are used for fertilizers. It also finds use in making nitric acid and other nitrates. Since it adsorbs water, it is not suitable for making gunpowder.

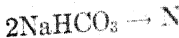
★ **444. Sodium Sulfate,  $\text{Na}_2\text{SO}_4$ .** This compound, which is a by-product from the manufacture of hydrochloric acid, is a colorless, crystalline compound. Its hydrate has the formula  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . It finds some use in medicine under the name Glauber's salt. Sodium sulfate finds some use in making cheap glass.

**445. Sodium Hydroxide,  $\text{NaOH}$ .** In the chapter on bases we learned that sodium interacts with water to form sodium hydroxide. This compound is produced commercially by the electrolysis of a solution of sodium chloride, the electrodes being in separate compartments so that the chlorine which is liberated at the anode does not by any chance come into contact with either the hydrogen or the sodium hydroxide at the cathode. Much of the sodium hydroxide is now made in Nelson cells or cells of the Vorce type. Sodium hydroxide is a white, crystalline solid. In purified form it is often cast in sticks. It is deliquescent, taking on first water from the air and then carbon dioxide, changing slowly into the carbonate. In water solution it forms one of

The sodium chloride interacts with the ammonium bi-carbonate and forms the bi-carbonate of soda and ammonium chloride:



If sodium carbonate is to be prepared, the sodium bi-carbonate is heated:



When the limestone is heated, calcium oxide is produced and break up a common cold in its be-



It is slaked by the addition of water. When it is used with soda

the acid interacts with the baking soda

$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$  dioxide. Sodium lactate is formed at

and the slaked lime is being soda also interacts with molasses

obtained as a by-product of ginger bread or cookies. Baking soda

$\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2$  and, or with some substance that will act

$\text{NaCl} + \text{NH}_4\text{HCO}_3$  solution, in the manufacture of baking

three common types:

$2\text{NaHCO}_3$  In this type of baking powder, cream

$\text{CaCO}_3$  potassium acid tartrate,  $\text{KHC}_4\text{H}_4\text{O}_6$ , sodium bi-carbonate to liberate carbon

$\text{CaO}$  f powder sometimes contains tartaric

$\text{CaO} + \text{H}_2\text{O}$  cream of tartar. Starch is used in all

$\text{Ca(OH)}_2 + 2\text{NH}_4\text{Cl}$  p the powder from deteriorating when

$\text{Ca(OH)}_2 + 2\text{NH}_4\text{Cl} \rightarrow \text{CaCl}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O}$  It adsorbs the moisture

FIG. 263. — A schematic diagram used to illustrate the possibilities of using by-products in a chemical manufacturing process.

left in the formation of the sodium bi-carbonate as represented in equation (2):

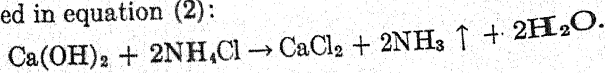


Figure 263 shows how the various by-products are utilized. The ammonia comes in part from the gas plant. The carbon dioxide comes from the limestone, as shown in Equation 4. The ammonium bi-carbonate that is formed in Equation 1 is used in Equation 2 to form the sodium bi-carbonate. Ammonia is liberated from

the ammonium chloride formed in Equation 2, by means of the calcium hydroxide formed in Equation 5. This ammonia is used again as in Equation 1. The carbon dioxide from Equation 3 is used again for forming more sodium bi-carbonate. The calcium chloride that is formed during the recovery of the ammonia is used as a binder on dirt roads to prevent an accumulation of dust.

**443. Sodium Nitrate,  $\text{NaNO}_3$ .** We have seen that extensive beds of sodium nitrate are found in the regions of western South America, especially in Chile. It is a colorless, crystalline, hygroscopic. Large quantities of sodium nitrate are used as fertilizers. It also finds use in making nitrates. Since it adsorbs water, it is used in gunpowder.

★ **444. Sodium Sulfate,  $\text{Na}_2\text{SO}_4$ .** This is a by-product from the manufacture of soda. It is a colorless, crystalline compound with the formula  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . It finds extensive use under the name Glauber's salt. Sodium sulfate is used in making cheap glass.

**445. Sodium Hydroxide,  $\text{NaOH}$ .** As we learned that sodium interchanges with hydrogen to form sodium hydroxide. This compound is produced especially by the electrolysis of a sodium chloride solution, the electrodes being in separate cells. During the war the tax which the Germans imposed on Brussels when they captured the city in 1914. (See Fig. 264.)

**448. Sodium Carbonate,  $\text{Na}_2\text{CO}_3$ .** This carbonate of sodium forms colorless crystals that have the formula  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . It finds extensive use in the manufacture of glass. Enormous quantities are used for softening hard waters, since it readily exchanges its sodium for the calcium or magnesium present in the hard water. When it hydrolyzes



in water, it gives an alkaline reaction. For that reason, it finds use in the laundry, under the name *washing soda*.

**449. Sodium Bi-carbonate,  $\text{NaHCO}_3$ .** This compound of sodium is generally known as baking soda. It interacts with acids and liberates carbon dioxide, either for use as a leavening agent or for use in extinguishing fires. It finds some use in medicine as an *antacid* to neutralize the excess acid that may at times be present in the gastric juice of the stomach. A half-teaspoonful of soda in water may thus counteract abnormal acidity and break up a common cold in its beginning.

Sour milk contains lactic acid. When it is used with soda as a leavening agent, the acid interacts with the baking soda and liberates carbon dioxide. Sodium lactate is formed at the same time. Baking soda also interacts with molasses and liberates carbon dioxide, which serves as a leavening agent in the baking of ginger bread or cookies. Baking soda is used with some acid, or with some substance that will act like an acid in water solution, in the manufacture of baking powders. There are three common types:

1. *Cream of tartar.* In this type of baking powder, cream of tartar, which is *potassium acid tartrate*,  $\text{KHC}_4\text{H}_4\text{O}_6$ , interacts with the sodium bi-carbonate to liberate carbon dioxide. This type of powder sometimes contains tartaric acid mixed with the cream of tartar. *Starch is used in all baking powders* to keep the powder from deteriorating when exposed to moist air. It adsorbs the moisture and keeps the powder dry. Since baking powders contain an acid, *sour milk* is not used with baking powder. Either water or *sweet milk* may be used.

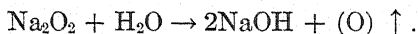
2. *Acid phosphate powders.* In this type of baking powder pure *mono-calcium phosphate*,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , is the acid salt used to set free the carbon dioxide from the baking soda.

3. *Sodium aluminum sulfate powders:* The so-called alums are double sulfates, made by crystallizing the sulfate of some

univalent metal with the sulfate of a trivalent metal. *Sodium aluminum sulfate*,  $\text{NaAl}(\text{SO}_4)_2$ , is the one used in baking powder. It hydrolyzes in water, and acts as an acid, since it is the salt of a strong acid. Thus it interacts with sodium bi-carbonate and liberates carbon dioxide.

Considerable discussion has arisen concerning the healthfulness of baking powders that contain one of the "alums." From investigations carried on by the Research Laboratories in Washington, there was no evidence of any harmful results from the use of sodium aluminum sulfate powders. Such powders were manufactured for the use of the United States Commissary Department during the World War.

★ 450. **Sodium Peroxide,  $\text{Na}_2\text{O}_2$ .** This compound, which is a yellowish-white powder, is formed by burning sodium in air. When it is added to water, it forms sodium hydroxide and oxygen.



Since nascent oxygen is liberated in this reaction, such a solution forms an excellent bleaching agent. Fibers bleach readily in an alkaline solution. Hence, sodium peroxide is to a considerable degree taking the place of hydrogen peroxide as a bleaching agent. It is sold under the name of *oxone*, to be used in preparing small quantities of oxygen. It finds considerable use as an oxidizing agent.

★ 451. **Sodium Thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ .** This compound, which is known as "hypo," is used in photography to dissolve any silver compounds that have not been changed or reduced by the action of light and a developer. Thus it "fixes" the plate so that it is no longer sensitive to light. It also serves as an "antichlor" to remove the last traces of chlorine used in bleaching.

452. **Sodium Cyanide,  $\text{NaCN}$ .** This white, crystalline solid is *extremely poisonous and must be handled with the greatest care*. With acids it interacts and forms the *deadly poisonous*

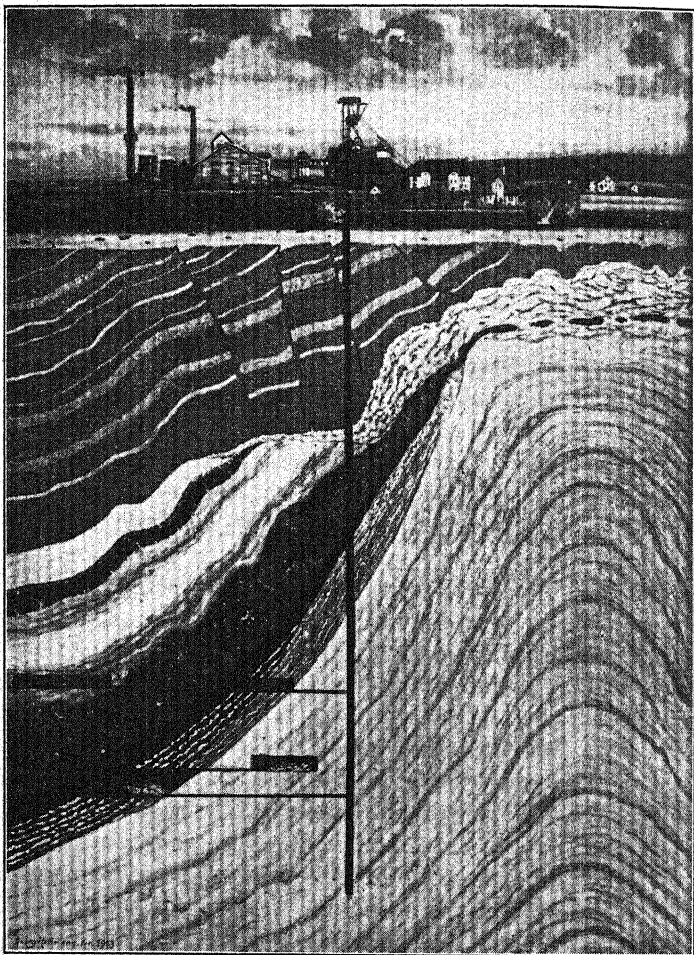
*hydrocyanic acid*, commonly called *prussic acid*. Used in this manner, sodium cyanide finds use in fumigating ships to destroy vermin, or in destroying insect pests on fruit trees. It is also used in extracting gold from its low grade ores, in preparing the electrolyte for plating with silver or gold, and in the process of case-hardening steel.

## B. POTASSIUM AND ITS COMPOUNDS

**453. Introductory.** The compounds of potassium resemble those of sodium so closely that they may often be used interchangeably. For example, either sodium chlorate or potassium chlorate may be used to prepare oxygen. Potassium compounds as a rule are rather more easily soluble than the compounds of sodium. When the World War shut off the supply of potassium compounds that had been imported from Germany, sodium compounds were used as substitutes and in many cases they are just as satisfactory. They are cheaper and they "go farther." The atomic weight of sodium is 23, and that of potassium is 39. If we are using potassium hydroxide, KOH, as a base, we must use 56 lb. in order to get 17 lb. of hydroxyl (OH); only 40 lb. of sodium hydroxide, NaOH, are needed to supply 17 lb. of hydroxyl.

★ **454. Metallic Potassium.** This metal was first extracted by Sir Humphry Davy by the electrolysis of potassium hydroxide. When he handed a lump of the metal to a friend, the man is said to have remarked: "Bless me, how heavy it is!" In reality, potassium is so light that it floats on water. It is slightly lighter than sodium. It is a soft, bluish-white metal that resembles sodium quite closely. It must be kept under kerosene or some other oil, since it is attacked by the oxygen, the moisture, and the carbon dioxide of the air. It is now extracted by the electrolysis of its fused hydroxide.

**455. Potassium Chloride, KCl.** At Stassfurt, Germany, there are found some remarkable deposits of the chlorides



*Courtesy of N. V. Potash Export My., Inc.*

FIG. 265. — A diagrammatic sketch showing the mineral deposits in a potash mine. The most important potash salts lie in the dark-colored strata. The thick white deposit is rock salt. These beds were probably formed by the slow evaporation of sea water when this area was shut off from the sea.

and sulfates of potassium, and of other soluble minerals. These beds, which are several hundred feet thick, have for years been the chief source of potassium compounds. Prior to the World War, Germany had a near-monopoly of potassium compounds, but some of these potassium deposits are in Alsace, which is now a part of France. (See Fig. 265.)

Potassium chloride is a white crystalline salt that is used as a starting point for making nearly all potassium com-

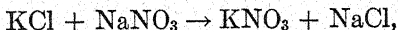


*Courtesy of N. V. Potash Export My., Inc.*

FIG. 266. — Crystallization of pure potash salts from the hot, concentrated solutions of the crude material.

pounds. It furnishes the bulk of the "potash" which is used for commercial fertilizers. Figure 266 shows the method of purifying the crude salts by crystallization.

**456. Potassium Nitrate,  $\text{KNO}_3$ .** This compound is made by mixing hot, concentrated solutions of sodium nitrate and potassium chloride. We would expect the reaction,



to be reversible, because all the products are soluble. But sodium chloride is much less soluble in hot water than the other compounds are, and it will separate as a crystalline solid which can be removed by filtration. This furnishes us with another example of the use of physical conditions to control the direction of a chemical reaction.

Potassium nitrate finds use in curing meats, such as corned beef and sugar-cured ham. Butchers sometimes make questionable use of potassium nitrate by sprinkling it over chopped meats so they will retain their bright red color. Potassium nitrate is a good oxidizing agent. Hence it finds use in fireworks and in making black gunpowder.

**457. Potassium Hydroxide, KOH.** The method of preparing potassium hydroxide is analogous to that of making sodium hydroxide. It resembles sodium hydroxide in its physical and chemical properties. In fact, the two compounds are so much alike that for most purposes one may be substituted for the other. In the soap industry, potassium hydroxide produces a *soft* soap, and sodium hydroxide yields a *hard* soap. Potassium hydroxide is the electrolyte used in the Edison storage battery.

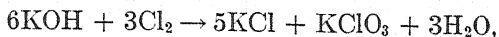
★ **458. Potassium Carbonate,  $K_2CO_3$ .** When wood burns, some potassium carbonate is formed. It may be extracted by *leaching* wood ashes with water. This method of making *lye* was at one time extensively practiced when our grandmothers boiled waste fats with *lye* for making soaps. It is still practiced in some localities. Considerable potassium carbonate is present in the mother liquor left after sugar crystals have been extracted from sugar beets. Wool perspiration, or *suint*, contains potassium carbonate, which is recovered from the waters used for washing wool. Thus we see that potassium compounds are closely related to animal and plant life. The most important use of potassium carbonate is in the manufacture of hard glass.

★ **459. Potassium Chlorate,  $KClO_3$ .** Two possible reactions

may occur when a halogen is passed into a solution of an alkaline hydroxide. When chlorine is passed into a *cold, dilute* solution of potassium hydroxide, for example, both *potassium chloride* and *potassium hypochlorite* are formed. The equation follows:



If, however, chlorine is passed into a *hot, concentrated* solution of potassium hydroxide, then *potassium chloride* and *potassium chlorate* are formed. The equation,



represents a typical reaction used in making *chlorates*.

Potassium chlorate is a white, crystalline solid, sparingly soluble in water. It is a vigorous oxidizing agent that finds use in making matches, explosives, and fireworks. Chlorate of potash tablets are used for sore throat.

★ **460. Other Potassium Compounds.** Potassium forms salts by its interaction with almost any acid. Scores of such compounds are known. The student will find it of interest to look over the list of potassium or sodium compounds as printed in a catalogue of chemicals. The compounds *potassium bromide*, KBr, and *potassium iodide*, KI, are both used in medicine and in photography. *Potassium acid carbonate*,  $\text{KHCO}_3$ , was at one time used as a leavening agent under the name of *saleratus*.

### C. FLAME TESTS

**461. Flame Tests for Metals.** If we dip a clean platinum wire into a solution of some sodium salt, and then hold the wire in the colorless flame of a burner, we find that the sodium compound volatilizes and imparts to the flame an *intense yellow* color. (See Fig. 267.) Potassium and its compounds, when treated in a similar manner, impart to



the flame a *violet* color. Lithium and its compounds give a *crimson* flame; barium compounds, a *yellowish-green* flame; calcium compounds, a *yellowish-red* flame. The flame test for metals is the simplest and quickest test we have. Un-

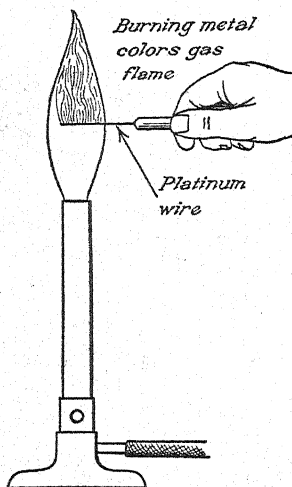


FIG. 267. — Some metals impart to the flame a characteristic color.

fortunately, this simple test is often valueless because the color of the flame may be obscured by the presence of other compounds. A spectroscope is necessary to distinguish an element when other elements are present.

**462. Use of the Spectroscope.** When rays of sunlight are passed through a triangular prism, a band of colors called a *spectrum* is produced. A white hot platinum wire produces a band of colors when its rays fall upon a prism. If we examine burning sodium through a spectroscope, which is an instrument for producing and examining spectra, we find that it gives a bright yellow band. This band is always formed in the same relative place in the spectrum; thus it serves to identify sodium. Potassium produces both red and violet lines. From the Spectrum Chart on the opposite page, we see the characteristic colors of hydrogen, nitrogen, and carbon. The stars and other heavenly bodies give characteristic spectra by means of which it is possible to determine the elements of

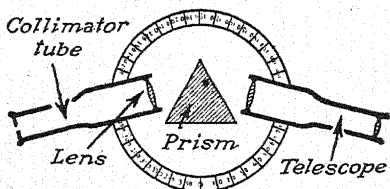


FIG. 268. — Spectroscope.

which they are composed. The method of spectrum analysis is the result of the work of two German chemists, Bunsen and Kirchhoff. By the use of the spectroscope, they discovered two new elements that belong to this family, *caesium* and *rubidium*. (See Fig. 268.)

## SUMMARY

The alkali metals are usually prepared by the electrolysis of their *fused* hydroxides. Their hydroxides are prepared by the electrolysis of *solutions* of their chlorides, which occur in nature. The hydroxides of these elements form very strong bases.

The *chlorides of sodium and potassium* are used in preparing other compounds of sodium and potassium. Potassium chloride is a valuable fertilizer.

*Sodium nitrate* is used as a fertilizer; it also finds use in making nitric acid and in preparing potassium nitrate for use in explosives.

The *carbonates of both sodium and potassium* find use in the glass industry. *Sodium carbonate* is commonly called soda ash or *washing soda*. It is an excellent material for softening hard water and as a cleansing agent in the laundry. *Sodium bi-carbonate* is used in fire extinguishers and in the manufacture of baking powders. Both carbonates of sodium are manufactured by the Solvay process.

*Sodium peroxide* is an important oxidizing agent used in the bleaching industry. *Sodium cyanide* is used in the metallurgy of gold, in making plating solutions, and as a poison.

When chlorine gas is passed into a *cold, dilute* solution of potassium hydroxide, the *hypochlorite* of potassium is formed. Potassium *chlorate* is formed when chlorine gas is passed into a *hot, concentrated* solution of potassium hydroxide.

Some metals impart to a flame a characteristic color by which the metals may be identified. The *spectroscope* is an instrument used to analyze the spectra produced by various substances when they are heated to incandescence. Elements present in very small quantities may be detected by means of the spectroscope. Each element produces characteristic lines in definite positions in the visible spectrum.

## QUESTIONS

## GROUP A

1. Why are sodium compounds so important in chemistry?
2. Discuss the commercial and industrial importance of sodium chloride.
3. How can you distinguish between sodium nitrate and potassium nitrate? Between sodium chloride and sodium nitrate?
4. In what laboratory exercises have the following compounds been used: sodium chloride, sodium nitrate, potassium chlorate, sodium carbonate, sodium hydroxide, and sodium bi-carbonate?
5. What methods can you suggest to keep table salt from "caking"?
6. Washing soda dissolves wool and it turns oak floors black. Under what circumstances may it be used as a cleansing agent?
7. If a manufacturer uses sodium carbonate in quantity, what advantage is it for him to buy calcined (strongly heated) sodium carbonate?
8. Why does a baker get more consistent results by the use of baking powder than he does by using sour milk and soda?
9. Explain how calcium chloride can be used to prevent clouds of dust arising from dirt roads.
10. Before adding the milk to the tomatoes in making cream of tomato soup it is a good idea to add a pinch of soda. Explain.
11. How do the salts of ammonium resemble those of sodium and potassium?
12. How does the solubility of sodium chloride in cold water compare with the solubility of potassium nitrate in cold water? How do their solubilities in hot water compare? What use is made of these differences?

## GROUP B

13. Why are water solutions of the carbonates of sodium alkaline? Which would you expect to be more strongly alkaline? Give a reason.
14. If sold at the same price per pound, which is the cheaper leavening agent, sodium bi-carbonate or potassium bi-carbonate?

15. What uses can be made of sodium peroxide?
16. What properties has a solution that is formed by passing water slowly through wood ashes? What name is given to the solution? For what is it used?
17. How would you proceed to prepare sodium bromide? Potassium iodide?
18. From Equation 3, page 515, would you expect that sodium bi-carbonate alone would act as a leavening agent? If so, is there any objection to its use?
19. One sometimes hears the statement that soda is used with sour milk to sweeten the milk. Correct the statement.
20. Why should sour milk not be used with baking powder in making biscuits?

## PROBLEMS

## GROUP A

1. How many pounds of nitric acid can be made from 100 lb. of potassium nitrate that has a purity of 80%?
2. How many grams of hydrochloric acid can be neutralized by 10 gm. of sodium hydroxide? How many grams of the same acid can be neutralized by 10 gm. of potassium hydroxide?

## GROUP B

3. If crystallized sodium carbonate,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , sells for 10¢ per pound, and  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  sells for 16¢ per pound, what is the cost in each case of one pound of anhydrous sodium sulfate?
4. How many liters of carbon dioxide can be liberated from 100 gm. of each of the following:  $\text{Na}_2\text{CO}_3$ ;  $\text{NaHCO}_3$ ; and  $\text{KHCO}_3$ ?

## SUPPLEMENTARY PROJECT

Prepare a report on the following topic:

1. The various sources of salt.

Reference: *New International Encyclopedia*.



## CHAPTER 32

### ALKALINE EARTH GROUP

#### Vocabulary

**Coquina.** A white shell-rock formed largely of the shells of the coquina clam.

**Calcareous.** Pertaining to limestone or calcium carbonate.

**Weathering.** The changing of solid bed rock to loose mantle rock.

**Pyrotechnical.** Pertaining to fireworks.

**Lycopodium.** One of the club mosses that produces yellowish spores, called lycopodium powder.

**463. General Family Characteristics.** The three elements, *calcium*, *barium*, and *strontium*, are very similar in their properties. *Radium* belongs in this family of elements, and it resembles them chemically. It has such unusual properties, however, that a separate chapter is given to the discussion of radium and its properties. The hydroxides of these elements are slightly soluble in water and they form strong bases. This family of elements is sometimes known as the *alkaline earth group*. The elements never occur free in nature. They may be prepared by the electrolysis of the fused chlorides. There is little demand for the metals, because their practical applications are limited. The elements in this family all have a valence of two.

#### A. CALCIUM

★ **464. How Calcium Is Extracted.** In preparing calcium, the compound calcium chloride is melted in a graphite crucible which serves as the anode. The cathode is an iron rod that dips into the molten chloride. The calcium is deposited on the end of the iron rod, which is raised out of the

molten mass by a screw mechanism as the calcium deposit lengthens. The deposit of calcium then serves as the cathode. The calcium chloride is kept molten by the heat produced by the resistance it offers to the passage of the electric current. This process is essentially the same as that devised by Robert Hare, an American chemist, who is credited with being the first successfully to isolate the metal. Sir Humphry Davy had, however, produced a very small quantity prior to the work of Hare.

★ 465. **Metallic Calcium.** This metal is silver-white in color. It is a little harder than lead, but its density is only about one-eighth as great. It may be kept in a stoppered bottle, but it tarnishes in moist air. It attacks water and liberates hydrogen, but more slowly than the alkali metals do. It is a good reducing agent. If heated above its melting point, it burns in oxygen, or in chlorine. The applications to which it is put are few, and the demand for the metal is small.

## B. COMPOUNDS OF CALCIUM

466. **Calcium Carbonate,  $\text{CaCO}_3$ .** This is one of the most abundant compounds of calcium, and also one of the most useful. It is found in various forms:

*Limestone* is the most important form of calcium carbonate. It is quarried in nearly every state in the United States. It was probably formed in past geologic ages from accumulations of shells from marine animals. Although pure calcium carbonate is white in color, or colorless when crystalline, the natural deposits are often colored gray, blue, red, or brown by the presence of organic matter or iron compounds. When first quarried, it is soft enough to be sawed or cut without much difficulty. It hardens somewhat after it has been quarried for a time. Limestone finds use as a building stone, especially for foundation work. It is fairly durable. With or without the addition of cement, lime-

stone finds extensive use for making, repairing, and ballasting roads. Enormous quantities are heated to produce *quicklime*. Limestone finds extensive use as a flux in the reduction of metals, especially of iron. We have already learned that it is one of the important raw materials used in the manufacture of *glass*, the *carbonates of sodium*, and *carbon dioxide*.

*Calcite* is a crystalline variety of calcium carbonate. Transparent, colorless specimens are known as *Iceland spar*.

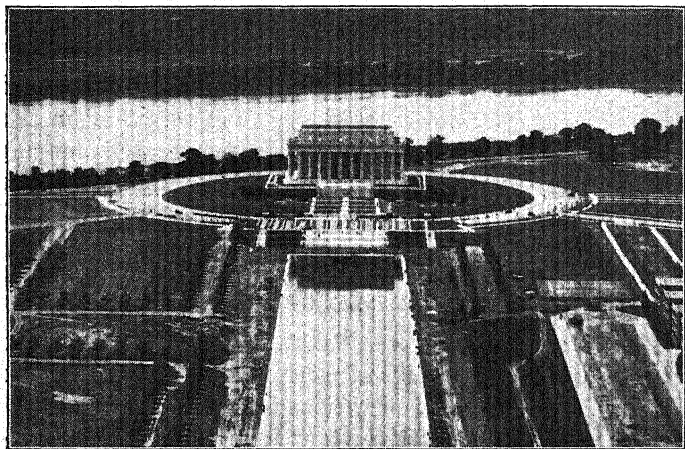


FIG. 269. — The Lincoln Memorial at Washington is built of fine marble.

The letters on a printed page appear double when viewed through *Iceland spar*. This phenomenon is known as double refraction. *Calcite* is used in the making of standard or normal solutions of acids, since the weight of acid needed to dissolve all the calcium carbonate in a pure sample can be calculated accurately.

*Marble* consists of fine grains of *calcite*. Originally it was probably deposited as limestone, and later changed by heat and pressure into marble. It takes a high polish, and it is



easy to cut or carve. Hence it finds use for making statuary, monuments, and as a finishing stone. One of the finest memorials ever erected to any man is the Lincoln Memorial Building in Washington. It is built entirely of marble and limestone. (See Fig. 269.)

Marble is cut from the quarries with channeling machines into blocks that weigh about 15 tons each. (See Fig. 270.) These blocks are hoisted from the quarries, and sawed with smooth iron bands, set in a horizontal frame which pulls the bands back and forth across the marble. Water carrying particles of sand flows continuously down over the block as the bands are drawn to and fro. (See Fig. 271.) These particles of sand really serve as teeth for the saws. In some cases circular saws, set with diamonds to serve as teeth, are used. After the sawing is done, the slabs are rubbed with sand and water to make them smooth. Afterwards they are rubbed to produce a high polish. The quarries at West Rutland, Vermont, are over 300 ft. deep, and they have a total underground space of more than 17 acres. Like limestone, marble occurs in a wide variety of colors.

*The shells* of such animals as clams, snails, and oysters consist largely of calcium carbonate. When the animals

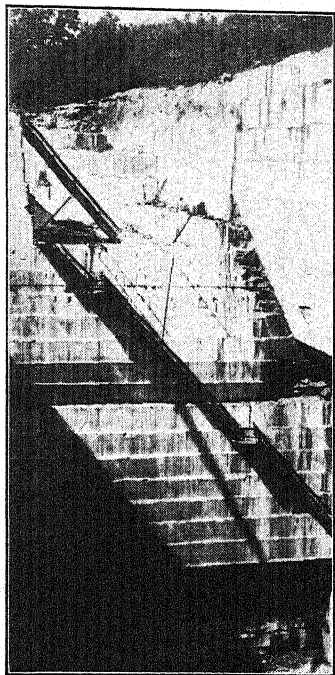


FIG. 270. — Marble quarry several hundred feet deep.

die, the shells may become firmly cemented together to form large masses of rock. Such processes are now taking place, and they also occurred in past geologic ages. Old Fort Marion, at Saint Augustine, Florida, is built of a shell rock called *coquina*. (See Fig. 272.) The oldest houses in America are built in part at least of such rock. The coral polyp

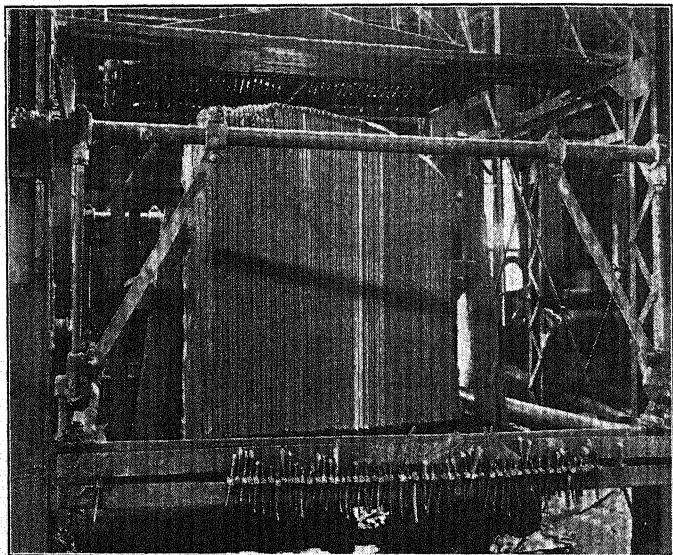
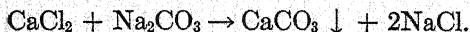


FIG. 271. — Sawing marble with toothless metal bands.

deposits limestone and builds *coral reefs and islands*. *Pearls* are composed of calcium carbonate. *Chalk*, such as the famous chalk-cliffs of England, is of geologic formation, consisting of the microscopic remains of small marine animals. Blackboard crayon is often composed of clayey material, and it should not be confused with calcareous chalk.

*Precipitated chalk* is an artificial calcium carbonate prepared by the action of sodium carbonate on calcium chloride.



It is soft and finely divided. Thus it forms a non-gritty scouring powder, suitable for tooth pastes and powders. As *whiting*, it is used as a filler in paints. Ground with linseed oil, it forms *putty*.

**467. How Caves or Caverns Are Formed.** In Section 110 we learned that water which has carbon dioxide in it will dissolve limestone. When the limestone is carried away by the water in which it is dissolved, caverns are formed. The

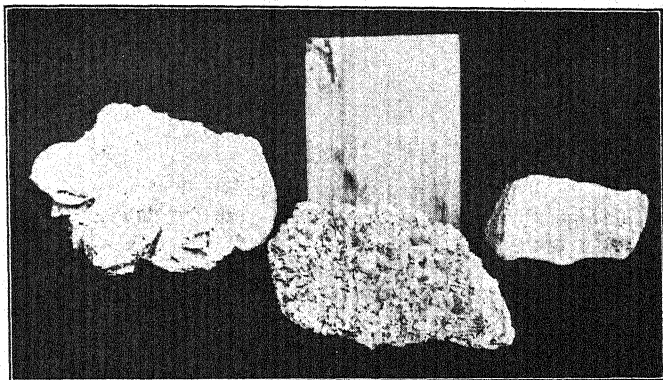
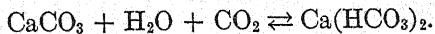


FIG. 272. — Varieties of calcium carbonate, including a slab of polished marble, fossil-bearing limestone (left), oölite (right), and coquina (center).

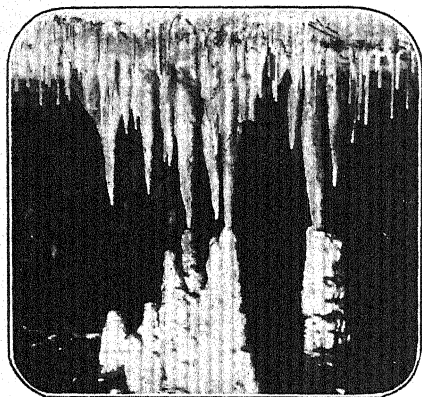
Luray Cavern in Virginia underlies an area of about 100 acres. The Mammoth Cave in Kentucky and the Carlsbad Cavern in New Mexico are famous for their size. If the earthy material above the cavern falls into it, a *limestone sink* is formed.

The chemical equation that represents the solvent action of a carbonated water on limestone is reversible.



Hence, drops of water that contain calcium bicarbonate in solution may, as they hang from the roofs of the caverns,

lose carbon dioxide and deposit the limestone in icicle-like masses called *stalactites*. Upon the floor of the cavern, further precipitation may build up masses of calcium carbonate that are called *stalagmites*. As the stalactites grow downward by the continued deposition of material and the stalagmites grow upward, they may meet and form columns,



*Salisbury's Physiography, by permission*

FIG. 273. — Stalactites and stalagmites in Marengo cave.

as shown in Fig. 273.

The Luray Cavern is famous for the beauty of its stalactites, columns, and stalagmites.

#### 468. How Calcium Oxide Is Made, $\text{CaO}$ .

If we heat limestone or marble to a high temperature, carbon dioxide is driven off as a gas, and calcium oxide remains. In the *short flame* process of making lime, the fuel is mixed with the lime-

stone in a furnace called a *kiln*. The ash from the fuel contaminates the product and the calcium oxide, or lime, is not very pure. Figure 274 is a diagram to show how lime is made in a *continuous action* kiln by the *long flame* process. Limestone is fed periodically into the kiln through a hopper. The fuel is burned on hearths outside the kiln and the flames and hot gases are pushed up through the limestone on the inside of the kiln. The lime, which is removed from the bottom of the furnace, is not contaminated with the ashes from the fuel.

A modern *rotary kiln* is shown in Fig. 275. Limestone or marble scraps are crushed to pieces no larger than a walnut, and fed into the upper end of a slowly rotating inclined

cylinder which may be 8 ft. in diameter and 125 ft. in length. As the lumps work their way along the kiln they meet the hot gases from the burning fuel, which is usually oil or gas. By the time they reach the lower end of the kiln, all the carbon dioxide has been driven off by the heat. The lime then drops into another rotating cylinder, in which it is cooled. Some of the lime is packed in barrels or drums for shipment as *quicklime*, but in many modern plants it is first *hydrated* or *slaked* and then bagged.

**469. Properties and Uses of Calcium Oxide.** Pure calcium oxide is a soft, white, non-crystalline compound. It is very refractory, melting or vaporizing only at the temperature of the electric arc. It unites chemically with water to form calcium hydroxide, or *hydrated lime*. The process is called *slaking*.



As the lime unites with water it swells up, and large quantities of heat are evolved. Wooden containers filled with quicklime will burst if the lime gets wet, and the heat from the chemical reaction may be sufficient to set the wood on fire.

If a lump of quicklime is exposed to the air, it will gradually absorb water, swell up decidedly, crack, and crumble to

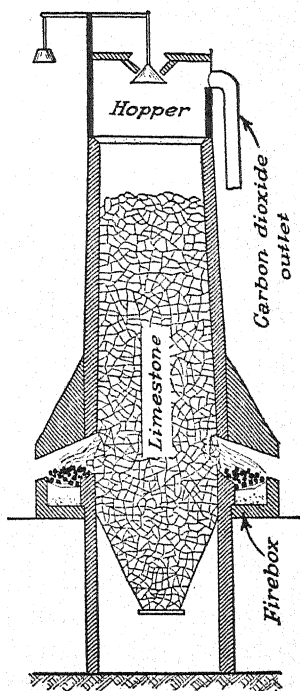


FIG. 274. — Sectional view of a vertical lime kiln.

a powder. It first forms calcium hydroxide, and then slowly takes carbon dioxide from the air and forms calcium carbonate. We have left a mixture of calcium hydroxide and calcium carbonate called *air-slaked lime*. It is not suitable for use in making mortar or plaster, but it is excellent for liming soils. Calcium oxide is used in the making of hydrated lime or slaked lime.

**470. Calcium Hydroxide,  $\text{Ca}(\text{OH})_2$ .** This product, which we have just learned is made by slaking calcium oxide, may be prepared by the mason who wishes to use it, or the cal-

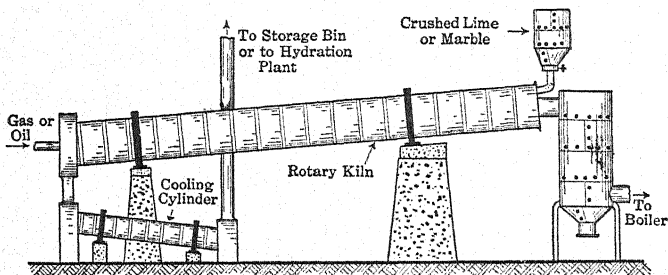


FIG. 275. — Rotary kiln for making lime.

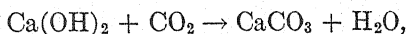
cium oxide may be hydrated at the plant where it is prepared. The latter practice prevents danger from fire and decreases air-slaking during transportation. In the hydrator, which consists of a rather shallow rotating cylinder, the quicklime is stirred mechanically with just enough water to combine with the amount of quicklime present. Some masons claim that lime slaked at the plant is not so plastic, and of course the consumer pays freight on some added water.

Calcium hydroxide is a white solid, only slightly soluble in water. Its water solution, which is known as *lime water*, is a strong base. Calcium hydroxide is the cheapest base that is known. Hence it finds extensive application, being used to remove hair from hides before tanning, in the *liming* of soils to neutralize excess acid, in the manufacture of



ammonia, in softening hard water, in making glass, and bleaching powder. Ellwood Hendrick says that if sulfuric acid is the "old horse" of chemistry, then lime is the "old mare." A suspension of calcium hydroxide in water, called *milk of lime*, is used for *whitewash*.

**471. Mortar and Plaster.** Large quantities of slaked lime are used in making mortar and plaster. *Lime mortar* consists of slaked lime, water, and sand. When mortar hardens or "sets," it first loses water by evaporation. Then carbon dioxide is slowly taken from the air, especially at the surface. From the equation representing the reaction,



we see that calcium carbonate and water are formed. Thus the calcium hydroxide gradually changes to a stony mass. It requires several years before all the hydroxide is changed to the carbonate. The sand mixed with the slaked lime serves several purposes: (1) It makes the mortar porous, thus giving better circulation of air. (2) It prevents undue contraction or shrinkage, and thus tends to prevent cracks and checks. (3) It makes the mortar harder and stronger, since it really forms hard grains cemented together by limestone when the mortar has thoroughly hardened. (4) Sand is cheaper than slaked lime, and it increases the bulk of the product.

*Plaster* does not differ much in composition from mortar. Sometimes hair or wood fiber is added to plaster to make it cling together better until hardening occurs. To make a harder mortar or plaster, cement is often substituted for part or all of the lime. *Cement mortar* will resist weathering to a greater degree than lime mortar. Walls plastered with cement mortar are not affected by water.

**472. Cement and Concrete.** In 1824 a Yorkshire brick-layer took out a patent for making Portland cement. He had heated chalk with clayey mud from the River Medway.



When his product hardened, it had the appearance of a limestone quarried near Portland. Hence the name "Portland cement." Several limestones are found which contain a considerable percentage of clay. When they are heated and then pulverized, they form what is now called *hydraulic cement*, or merely *cement*. Such a cement hardens under

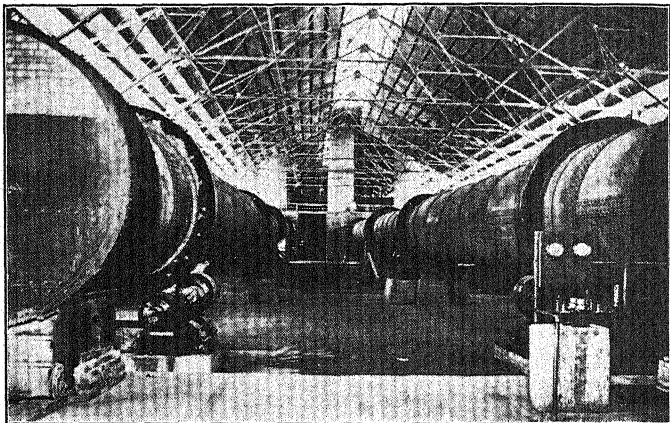


FIG. 276. — Rotary cement kilns.

water. Rocks that form cement in this manner are known as *natural cements*.

The present practice is to make an artificial cement by mixing limestone and clay in the proper proportions, to heat the mixture until it just begins to melt and form a clinker, and then grind the product to a very fine powder. The original mixture is ground, and then heated in a rotary kiln very similar in construction to a rotary lime kiln. (See Fig. 276.) Powdered coal, gas, or oil may be used as a fuel. By the time the mixture reaches the lower end of the kiln, it has been heated until it begins to melt. The clinker that leaves the kiln is ground so fine that at least 92% should pass through a 100-mesh sieve. To prevent too rapid setting,

2 or 3% of gypsum is usually ground with the clinker. The strength of cement mortar and of concrete seems to depend to a large extent upon the fineness of the finished product.

The hardening of cement is not understood. The first step appears to be partially due to the union of the components with water to form hydrates. Some believe that the action is colloidal, because it is possible to make a gel

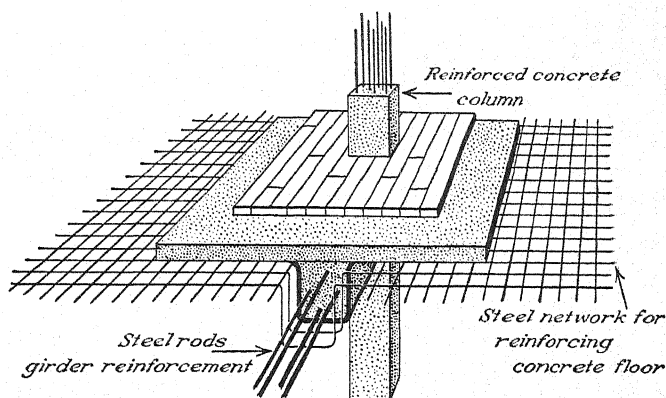


FIG. 277. — This sketch shows how steel rods are used to reinforce columns, girders, and floors.

by agitating very fine cement with water, and it has been shown that a very fine powder is stronger than a coarse one.

Concrete is made by mixing together *cement*, *water*, *sand*, and *crushed stone*. For driveway foundations, cinders are sometimes substituted for crushed stone. When concrete hardens or “sets,” it forms a very hard, compact mass. Thus it is suitable for making building blocks, foundation walls, garage and cellar floors, sidewalks, streets and roads, bridges, viaducts, dams, walls for canal locks, stucco, and for numerous other purposes. It is well to remember that it is moderately strong during the initial set, and that it weakens after a week or ten days. After about two weeks another change occurs. Then it becomes stronger and harder again.

*Reinforced concrete* is concrete that is strengthened by embedding in it rods of iron or steel. (See Fig. 277.) It is extensively used in structural work. (See Fig. 278.) Concrete is sometimes applied by means of an atomizer or cement gun. Figure 279 shows the use of such a gun for spraying the walls along a railroad cut. The United States produces about 100,000,000 barrels of cement annually. As timber

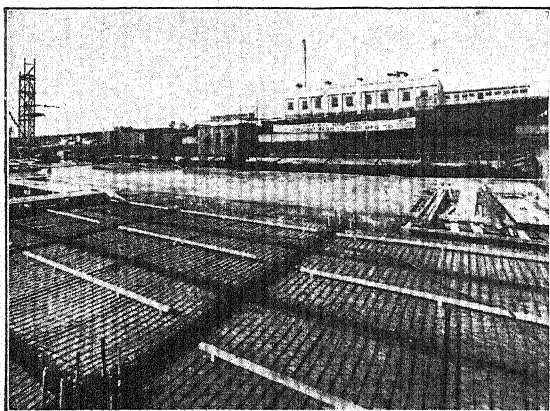


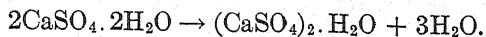
FIG. 278. — Steel wire in position for reinforcing concrete.

becomes scarce and the prices continue to increase, the applications of cement become more varied and the quantity manufactured continues to increase. Pebbles and cement mortar are used for making *stucco*, which is used for making the walls of buildings.

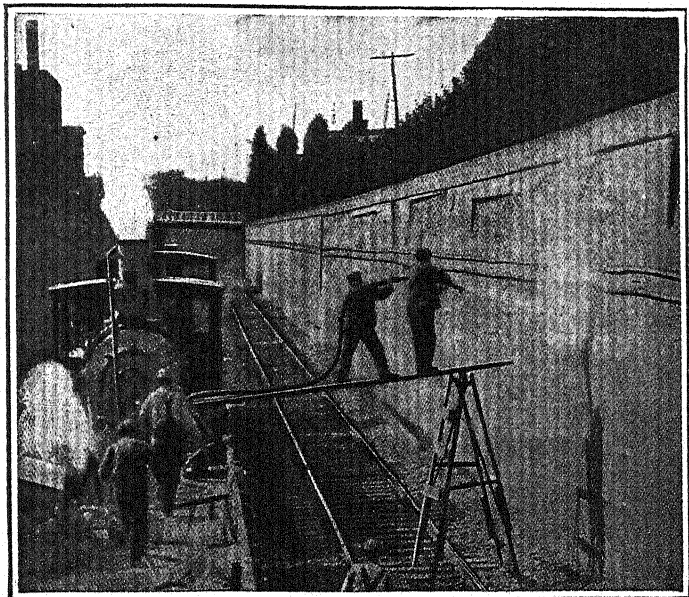
**473. Calcium Sulfate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .** Calcium sulfate occurs in nature in the mineral *gypsum*, which is found in Kansas, New York, Ohio, and Michigan. Transparent crystals of gypsum are known as *selenite*. A white opaque variety, known as *alabaster*, is used for making statuary. It is durable, and since it is so soft that it can be scratched with the thumb nail, it is one of the easiest minerals to carve.

When gypsum is heated to a temperature of  $110^\circ$  to  $130^\circ \text{C.}$ ,

it loses part of its water of crystallization, and forms a white substance known as plaster of Paris.



When plaster of Paris is mixed with water, it sets rapidly by taking on water and forming crystals. It thus hardens to a



*Permission of Scientific American*

FIG. 279. — Concrete atomizer in operation.

white solid that finds use in making casts, in plastering where it is mixed with lime to form a very white coating, and in making a decorative stucco, which also contains glue and stone. Large quantities are used in making wall-board or plaster board.

Impure gypsum finds use as a fertilizer under the name of *land plaster*. It is sometimes employed to counteract the

"black alkali" that forms in some arid soils. Calcium sulfate also finds use in calcimining, and as a filler for paper and paints.

**474. Bleaching Powder,  $\text{CaOCl}_2$ .** This compound is made by passing chlorine over thin layers of freshly prepared calcium hydroxide.

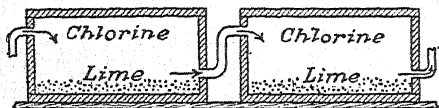


FIG. 280. — Chambers for making bleaching powder.

The chlorine enters the top of the chamber (Fig. 280), where it is absorbed by the calcium hydroxide.

Any unabsorbed chlorine passes on to the next chamber. The chamber is aired, and the bleaching powder is packed into metal cans or drums. The product is not very stable and gas is slowly evolved. Enough gas may accumulate to expel some of the grayish white powder forcibly when a can is opened. Care should be used to protect the eyes when opening cans of "chloride of lime" that have stood for some time. The moisture and carbon dioxide from the air act upon bleaching powder with the evolution of *hypochlorous acid*,  $\text{HClO}$ . Hence it is a good disinfectant. Large quantities are used for purifying water supplies, as a disinfectant, and in the bleaching industry.

★ **475. Other Calcium Compounds.** Several calcium compounds have already been studied. *Calcium phosphate*,  $\text{Ca}_3(\text{PO}_4)_2$ , used for making fertilizer; *calcium carbide*,  $\text{CaC}_2$ , a product of the electric furnace, used for making acetylene; *calcium cyanamide*,  $\text{CaCN}_2$ , used as a fertilizer and for making ammonia; and *calcium chloride*,  $\text{CaCl}_2$ , used as a dehydrating agent. *Calcium bi-sulfite*,  $\text{Ca}(\text{HSO}_3)_2$ , is a compound which finds extensive use in the making of print paper.

### C. BARIUM AND STRONTIUM

★ **476. Barium and Strontium.** These elements are found in nature as sulfates and as carbonates. *Barium sulfate*,

$\text{BaSO}_4$ , is a white heavy solid that finds use in a variety of industries. It is used as a filler in making heavy paper, and also in paints. Formerly it was considered an adulterant in paints, but it has been shown that it increases the durability and wearing qualities of paints. Considerable quantities of barium sulfate are being used in making *lithopone*, a white pigment. The gray paint used for our battleships contains about 45% of barium sulfate. *Barium peroxide*,  $\text{BaO}_2$ , is a vigorous oxidizing agent; it is used in making hydrogen peroxide. *Barium nitrate*,  $\text{Ba}(\text{NO}_3)_2$ , is a white crystalline solid. Since barium compounds impart a yellowish-green color to the flame, they find considerable use in making flares and other fireworks. The nitrate is generally used.

*Strontium* imparts a bright red color to the flame. Therefore its compounds are used as red fire in pyrotechnical displays. *Strontium nitrate*,  $\text{Sr}(\text{NO}_3)_2$ , mixed with powdered shellac and lycopodium powder, makes a beautiful red light for tableaux. The oxides of barium and strontium are used to coat the platinum alloy filament in vacuum tubes. A single layer of barium atoms on the surface of the alloy increases the yield of electrons more than 100,000,000 times that produced by the alloy alone.

## SUMMARY

*Calcium*, *barium*, and *strontium* are known as the alkaline earth group of metals. Their bases are strong alkalis. Each element has a valence of 2.

*Calcium* may be extracted by the electrolysis of the fused chloride. It is a silver-white metal that attacks water slowly, liberating hydrogen.

*Calcium carbonate* is used as limestone for building purposes, as a flux, in making glass, for producing carbon dioxide, and in the manufacture of quicklime.

*Calcium oxide*, or quicklime, is a soft, white solid that unites with water to form the base calcium hydroxide.

When a cheap base is needed for industrial operations, calcium hydroxide is generally used. For softening hard water, for removing hair from hides, for making ammonia and bleaching powder, and in the preparation of mortar, calcium hydroxide is used extensively.

*Mortar* is a mixture of slaked lime, sand, and water. Cement is often used to take the place of part or all of the lime in making mortar. Hence we have lime mortar and cement mortar. Plaster differs little in its composition from mortar.

*Cement* is prepared by heating a mixture of *calcium carbonate* and *clay* and then reducing the product to a very fine powder. With sand, crushed stone, and water, it forms *concrete*, a substance largely used for building materials. Concrete may be reinforced by having embedded in it bars of iron or steel.

*Calcium sulfate* is used as a fertilizer and in the manufacture of plaster of Paris.

*Barium* and *strontium* compounds are used in the manufacture of fireworks.

## QUESTIONS

### GROUP A

1. Why do the walls of freshly plastered houses remain damp for some time?
2. Why is air-slaked lime not desirable for making mortar?
3. What action occurs when marble is strongly heated? Write the equation.
4. Does marble make good lime? Is it ever used for this purpose?
5. Compare the "setting" of mortar, plaster of Paris, and cement.
6. Could barium hydroxide be substituted for calcium hydroxide as a base?
7. How can the flame test be used to identify sodium, potassium, barium, and strontium?
8. Why should care be taken to protect the eyes when opening cans of "chloride of lime"?



9. Explain how the building trades would suffer if deprived of calcium compounds.

10. Write the equation to represent the reaction between sodium carbonate and calcium sulfate that occurs during the softening of "permanent" hard water.

11. Write the equation to represent the reaction that takes place when slaked lime is added to "temporary" hard water that contains calcium bicarbonate.

12. Quite often lime water is added to milk given to bottle-fed babies. Explain.

GROUP B

13. Would limestone be completely converted into lime by heating it in a closed tube? Explain.

14. Why does a wood fire aid the hardening of the plaster in a new house?

15. Why does blowing air or steam into a lime kiln hasten the production of lime?

16. What is meant by air-slaked lime? Write the equations to show how it is formed from quicklime.

17. Suppose you had a truck-load of quicklime in wooden barrels that were not water-tight. If they started to burn when you got caught in a thunderstorm, how would you put out the fire?

18. Suppose you have separate samples of "temporary" and "permanent" hard waters. How would you proceed to soften each one? Write the equations.

19. If you were given a sample of hard water that contains calcium sulfate and magnesium bicarbonate, how would you proceed to soften such a water?

20. What is the meaning of the term "hydraulic cement" and why is it used?

21. A large chemical plant at Lake Charles, Louisiana, manufactures the hydroxide and the carbonates of sodium. Oyster shells are used as raw materials. They are heated in a rotating kiln some 12 to 14 feet in diameter and 360 feet long. What is the chemical formula of the solid product formed?

22. What gas is collected in the process of No. 21? Write the equation for the reaction.

## PROBLEMS

## GROUP A

1. How many pounds of calcium oxide can be obtained from one ton of limestone, 95% pure? How many pounds of slaked lime will it make?
2. How much weight will 200 lb. of gypsum lose when it is converted into plaster of Paris?

## GROUP B

3. Starting with calcium carbonate, write all the equations for the preparation of calcium oxide, calcium hydroxide, and calcium chloride. If you started with 250 gm. of pure calcium carbonate, how many cubic centimeters of hydrochloric acid containing 38% HCl would be needed to convert the carbonate into the chloride? One c.c. of hydrochloric acid weighs 1.2 gm.
4. How many liters of carbon dioxide are formed by heating 540 gm. of limestone that contains 10% impurity?

## CHAPTER 33

### THE MAGNESIUM FAMILY

#### Vocabulary

**Malleable.** Capable of being hammered or rolled into sheets.

**Ductile.** Capable of being drawn into wire.

**Spelter.** The name given to commercial zinc.

**Emetic.** A substance used to induce vomiting.

**Actinic.** Those rays present in the sun's rays that are capable of producing a chemical effect.

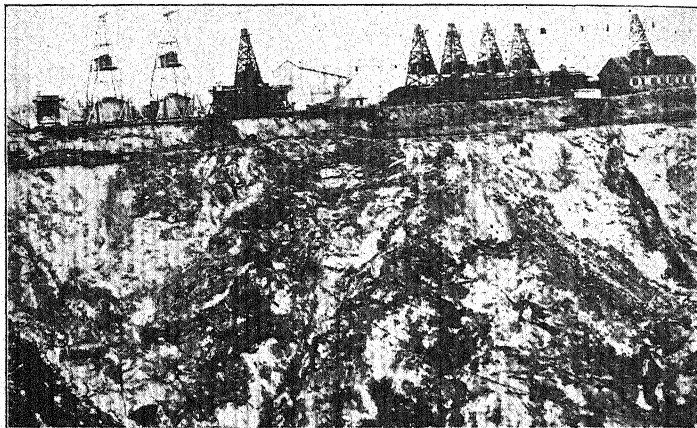
**Fouling.** Growth of barnacles and other marine animals on the hull of a ship.

**477. Introductory.** The magnesium family of elements includes: *magnesium*, *zinc*, *cadmium*, and *mercury*. The resemblance that is so marked in the families of elements that we have studied is not so close in this family. For example, in many respects magnesium is more like calcium than it is like zinc. In some respects it is much like zinc in its chemical properties. Mercury is like copper in some of its chemical properties. Magnesium is an active metal, but mercury is very inactive. The usual valence of the elements in this family is 2, but mercury sometimes has a valence of only 1.

#### A. MAGNESIUM

**478. How Magnesium Is Found in Nature.** *Magnesium sulfate* occurs in some of our western states and in British Columbia. About 30 tons of 95% magnesium sulfate are mined daily in Washington. *Dolomite* is a double carbonate of calcium and magnesium. It forms an excellent building

stone. It is widely distributed in the United States and in Europe. In the Tyrols of Austria there are mountain ranges made up almost wholly of dolomite. *Talc* and *asbestos* are magnesium silicates. Asbestos is mined extensively in the province of Quebec. (See Fig. 281.) It is a remarkable mineral that can be woven into cloth. It finds use for making shingles, furnace and steam-pipe coverings, auto-



*Photo by Ewing Galloway*

FIG. 281. — The King Pit asbestos mines at Thetford Mines, Quebec.

mobile brake bands, fireproof clothing and curtains, electrical insulation, and motion-picture booths. (See Fig. 282.) *Carnallite*, a double chloride of potassium and magnesium, is found in the Stassfurt deposits.

★ 479. **How Magnesium Is Extracted.** The element magnesium is extracted by the electrolysis of the fused chloride, or of carnallite, in an iron crucible that serves as the cathode. A graphite rod is used as the anode. The metal is usually powdered for the market or drawn into wire or ribbon.

**480. Properties of Magnesium.** A silver-white metal, magnesium is only 1.75 times as dense as water. It is ductile and malleable when heated. Magnesium is not acted upon by dry air, but in moist air a coating of basic carbonate forms on its surface. This coating does not scale off the way iron rust does, but it protects the metal underneath from further tarnishing. A metal that forms such a non-porous, non-scaling coat is said to be "self-protective." In air, magnesium burns readily and forms a mixture of the oxide and some nitride,  $Mg_3N_2$ . It is one of the few metals that combines directly with nitrogen. Magnesium decomposes hot water slowly with the liberation of hydrogen. All common acids attack the metal and form salts.

**481. Uses of Magnesium.** When magnesium burns, it produces

a dazzling white light that is rich in *actinic rays*. Such rays are active in producing a chemical effect, upon a photographic plate, for example. Hence, powdered magnesium mixed with an oxidizing agent has been used for flashlight powders. It finds use for making flares and in fireworks. During the World War it was used for flares and star-shells.

Magnesium forms with aluminum alloys that are light and strong. *Magnalium* and *dowmetal* are examples of such alloys. They find use in airplane and automobile parts, for the beams of delicate chemical balances and for novelty articles.

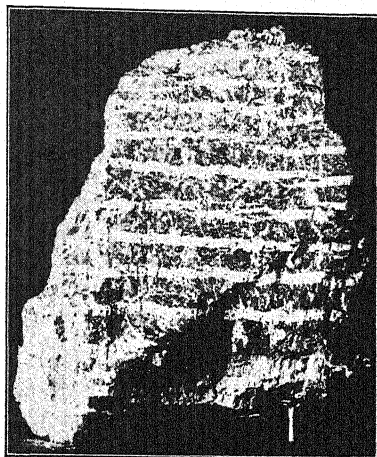


Photo by Ewing Galloway

FIG. 282. — Note the fibrous structure of the asbestos. The white strata are the asbestos fibers.

**482. Magnesium Oxide,  $\text{MgO}$ .** This is a white, refractory compound that finds extensive use for lining furnaces and crucibles, and for making fire brick. It is made by heating *magnesite*,  $\text{MgCO}_3$ , a mineral found extensively in nature.



The reaction is analogous to that for making quicklime. *Magnesia*, a common name for the oxide, unites with water and forms *magnesium hydroxide*,  $\text{Mg}(\text{OH})_2$ . The hydroxide is not very soluble in water, but a *suspension* of the oxide and hydroxide is used as a laxative and antacid under the name of "milk of magnesia." The oxide and the chloride of magnesium are used with wood fiber or asbestos to form a compound that finds use for artificial stone floors.

**483. Magnesium Carbonate,  $\text{MgCO}_3$ .** The carbonate found in nature is used for lining furnaces. When one adds

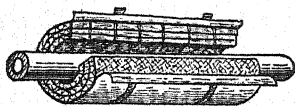


FIG. 283. — Heat insulator.

a soluble carbonate to a compound of magnesium, the normal carbonate is not precipitated. One always gets one of the basic carbonates of magnesium. One of these basic carbonates is a

soft, light, fluffy powder that finds use in making tooth pastes, silver polish, and cosmetics. It is called *magnesia alba*. A crude product that has an exceedingly loose structure is used for covering steampipes. It is so light that it is about 90% pores. It is an excellent heat insulator, which is sold under the trade name of "85 per cent magnesia." (See Fig. 283.)

★ **484. Magnesium Chloride,  $\text{MgCl}_2$ .** This compound, which is used in making artificial stone for flooring, is present in sea water. When sea water is heated, this chloride hydrolyzes and some hydrochloric acid is formed. For that reason sea water cannot be used for steam engines, because the acid that is formed attacks the boilers, and the mag-

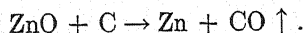
nesium hydroxide that is formed at the same time is deposited as scale.

**485. Magnesium Sulfate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ .** This compound of magnesium was first extracted from the waters of a mineral spring near Epsom, England. Hence it is known as *Epsom salts*. It is used in medicine as a laxative. It finds some use in the dye industry.

### B. ZINC

**486. Occurrence.** The United States produces about one-half of the zinc that is produced in the world. Oklahoma, New Jersey, Montana, Kansas, and Missouri are the most important zinc-producing states. A sulfide of zinc, known as *sphalerite*, or zinc blende, is an important ore, but the metal is also extracted from a carbonate ore known as *smithsonite*, and from certain silicates of zinc. *Franklinite*, an oxide of zinc that is mixed with the oxides of iron and manganese, is found in New Jersey.

**487. How Zinc Is Extracted.** The method of extracting zinc is a simple one of reduction. The ore is converted into the oxide by roasting, then mixed with powdered coal, and heated in earthenware retorts. (See Fig. 284.) The following equation represents the reaction that occurs:



The zinc vaporizes and it is condensed in iron or earthenware receivers. Some of the zinc is deposited as *zinc dust* in the upper part of the receivers. The liquid zinc is drawn off at the bottom of the receiver and cast in molds. The *spelter* thus formed contains arsenic, carbon, and cadmium as impurities. It may be purified by distillation. Sometimes it is purified by electrolysis.

**488. Properties of Zinc.** Zinc is bluish-white in color. At ordinary temperature it is somewhat brittle, but at a



slightly increased temperature it becomes malleable and ductile. If heated, it may be rolled or drawn; when it is subsequently cooled, it does not become brittle.

Zinc burns in air with a bluish-white flame and forms zinc oxide. Dry air does not affect zinc, but moist air attacks it and forms a basic carbonate. The tarnish that forms is adherent. Hence, zinc is a "self-protective" metal. *Chemically pure* zinc is attacked slowly by acids, but ordinary acids

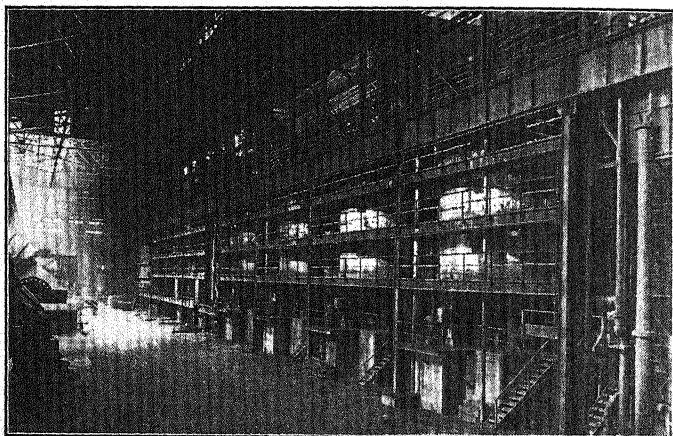
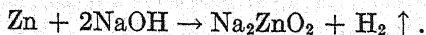


FIG. 284. — Retorts used in extracting zinc.

readily attack zinc that contains a trace of impurity. The active bases, sodium and potassium hydroxides, dissolve zinc with the evolution of hydrogen. Soluble *zincates*, which may be considered salts of zincic acid, are formed, as represented by the following equation:



**489. Uses of Zinc.** Of course we would expect to find that zinc is the starting point for the making of its compounds. Enormous quantities are used in making zinc oxide, for example.

Large quantities are used for making *galvanized iron*. The iron is thoroughly cleaned by "pickling" it in an acid bath to remove scale and tarnish. Then it is covered with zinc by the use of any one of three methods: (1) It may be dipped into a vat of molten zinc. (See Fig. 285.) Wire is galvanized by drawing it through a bath of melted zinc, as shown in Fig. 286. The zinc that adheres to the iron after dipping is beautifully crystalline. (2) Sometimes zinc is

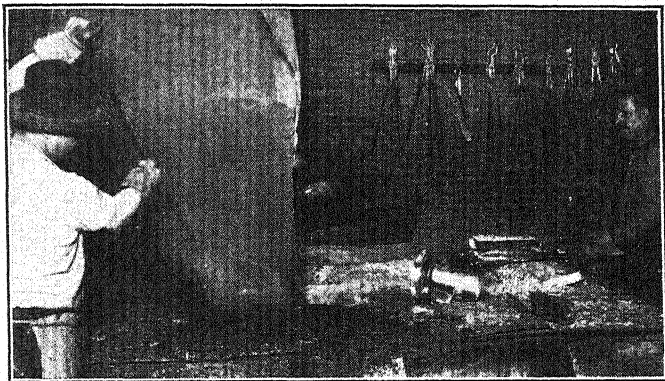


FIG. 285. — The workman at the left shoves the article to be galvanized into the left portion of the vat and it is removed by the other man. The molten zinc in the left compartment is covered with a layer of sawdust and ammonium chloride.

plated on the surface of the metal by means of electrolysis. This method is more costly than the dipping process. (3) Sometimes the zinc is heated to vaporize it. Then the zinc vapor is permitted to condense upon the surface of the object to be coated. This process is known as *sherardizing*.

Let us turn to the replacement series and observe the position of zinc in the series. We find it near the electro-negative end of the series. No metal is so well-fitted as zinc for use as the negative element in voltaic cells. Practically

all types of voltaic cells use zinc as the negative plate. The metal cylinder of the dry cell is composed of zinc.

Since all the soluble salts of zinc are poisonous, acid foods should not be stored in galvanized iron containers.

**490. The Alloys of Zinc.** The most important alloy of zinc is *brass*, which contains zinc and copper. *Bronze* contains copper and tin; sometimes zinc is added. *German*

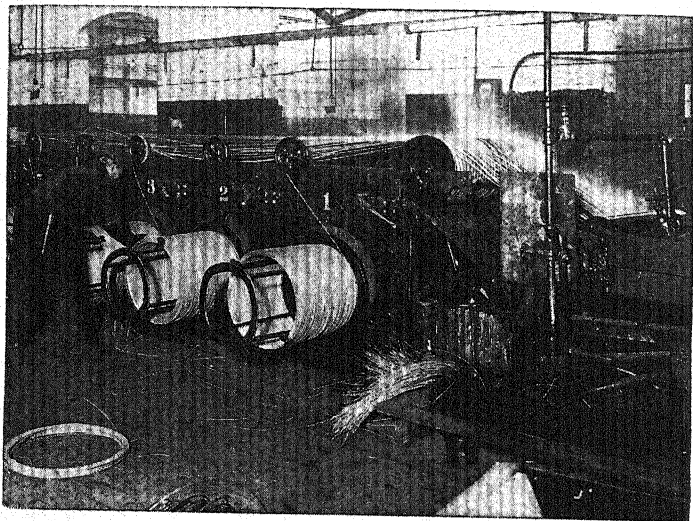


FIG. 286. — Iron wire is unrolled, passed through a vat of molten zinc, and then re-rolled after the galvanizing process.

*silver*, or *nickel silver*, is an alloy containing copper, nickel, and zinc.

**491. How to Test for Zinc.** When zinc is heated on the surface of a charcoal block, or a block made from plaster of Paris, by using the oxidizing flame of a blowpipe, the oxide formed appears a canary-yellow color when hot, and white when cold. Zinc compounds are generally converted into the oxide by such heating, and behave in the same manner. If the white residue is moistened with a drop or two of

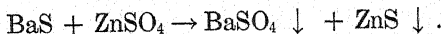
cobalt nitrate solution and again heated, a *dark-green* residue is formed. This makes a fairly satisfactory *test for zinc*.

**492. Zinc Oxide,  $\text{ZnO}$ .** The oxide of zinc may be prepared by roasting the sulfide ore, or it may be prepared by burning the metal itself. It is a white solid that is used as a paint base, as a filler in rubber for automobile tires, in oilcloth, and for glazes and enamels. *Zinc ointment* contains zinc oxide and zinc stearate in a base of some kind of grease. The advantages and disadvantages of zinc oxide as a paint base are discussed in a later chapter.

**493. Zinc Chloride,  $\text{ZnCl}_2$ .** This salt of zinc, which is a white, deliquescent solid, finds use in preserving wood that is to be used in contact with the earth, such as railroad ties, fence posts, etc. Sometimes it is used with creosote. Such a doubly treated post or tie is very resistant to decay. Zinc chloride is used as a soldering fluid. Zinc chloride attacks wood fiber and converts it into cellulose hydrate, a product that can be pressed into any desired shape and then dried. This strong, tough product, which is called *fiber board*, or "vulcanized fiber," is employed in making boxes, trunks, washers, pails, and insulating materials.

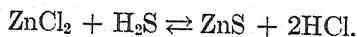
★ **494. Zinc Sulfate,  $\text{ZnSO}_4$ .** This compound of zinc is a white crystalline solid used in making *lithopone*, a paint base. It also finds use in making cotton print goods, as a disinfectant, and to some extent in medicine as an emetic.

**495. Zinc Sulfate,  $\text{ZnS}$ .** This is the only common sulfide that is white in color. If solutions of barium sulfide and zinc sulfate are mixed, two white insoluble products are precipitated together, zinc sulfide and barium sulfate.



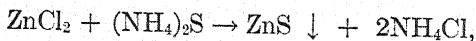
If this mixture of precipitates is heated and then plunged into cold water, the product formed may be ground with linseed oil to form an excellent paint base. It is a brilliant white of excellent covering power.

★ If we try to precipitate zinc sulfide by adding hydrogen sulfide to a solution of zinc chloride, the precipitation is incomplete:



Zinc sulfide is insoluble in water, but in the reaction shown above, hydrochloric acid is being formed at the same time the zinc sulfide is being precipitated. When the concentration of the hydrogen ion becomes sufficiently great, no more zinc sulfide can be precipitated and equilibrium occurs.

If we add to a solution of zinc chloride some ammonium sulfide, then the precipitation of the zinc sulfide is complete,



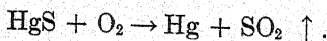
because we have no hydrogen ions formed that will cause the reaction to reverse.

#### C. CADMIUM

★ 496. Cadmium, Cd. This element is usually found in nature associated with zinc. It resembles magnesium and zinc in its properties. Cadmium finds use in making some of the fusible alloys. This metal forms a durable coating for iron and steel. Cadmium sulfide, CdS, is a fine yellow compound that finds use as an artist's color.

#### D. MERCURY

497. How Mercury Is Found in Nature. Small quantities of mercury are found uncombined, but the chief ore is mercuric sulfide, HgS, a red mineral known as *cinnabar*. Spain, Italy, California, and Texas produce the bulk of the mercury for the world's supply. The metal is so easily reduced that it was known to the ancients. It is extracted from cinnabar by roasting the ore.



Mercury is purified by distillation.

**498. Physical Properties.** Mercury is a heavy, silver-white metal with a metallic luster. It is the only metal that is liquid at the ordinary temperature. It is commonly called *quicksilver*. Mercury freezes at about  $-39^{\circ}\text{C}$ ., and it boils at  $357^{\circ}\text{C}$ . It is 13.6 times as dense as water. Hence such common metals as zinc, iron, copper, tin, and lead float on mercury. Gold and platinum are so dense that they sink in mercury.

**499. Chemical Properties.** Mercury does not tarnish when exposed to the air. If heated, however, it slowly changes to a red powder, mercuric oxide,  $\text{HgO}$ . The student will recall that Lavoisier prepared this red powder in his experiment to explain combustion, and that Priestley prepared oxygen by heating the powder. Since mercury stands below hydrogen in the replacement series, it cannot displace hydrogen from hydrochloric acid. Hydrochloric acid does not attack it at all. The strong oxidizing acids, nitric and sulfuric, attack mercury and form salts of the respective acids.

**500. Uses of Mercury.** The following properties of mercury make it suitable for use in thermometers: (1) It has quite a low freezing point and a high boiling point; (2) It has a much higher coefficient of expansion than glass; (3) Its expansion is quite uniform, especially between  $0^{\circ}\text{C}$ . and  $100^{\circ}\text{C}$ . To illustrate, a column of mercury increases the same amount when heated from  $20^{\circ}$  to  $21^{\circ}\text{C}$ . that it does when heated from  $40^{\circ}$  to  $41^{\circ}\text{C}$ . Mercury is suitable for use in barometers since it has so high a specific weight. Mercury is a fairly good conductor of electricity; it is convenient for such use when a good contact is desired. Mercury finds some use in the collection of soluble gases and in certain kinds of air-pumps. Mercury is also used in the various types of mercury vapor arc lamps and in arc rectifiers, and in the manufacture of fulminating mercury.

With many other metals mercury forms alloys known as

*amalgams.* In extracting gold and silver, the powdered mineral containing these precious metals is treated with mercury to form amalgams from which the gold and silver may be recovered by distilling the mercury. An amalgam consisting largely of silver, tin, and mercury is used for filling teeth. The zincs used in voltaic cells are amalgamated with mercury to prevent local action between zinc and its impurities. Amalgams appear to be solutions of metals in mercury, or in some cases definite compounds.

**501. Compounds of Mercury.** Mercury forms two classes of compounds: *mercurous*, in which the valence of the element is 1; and *mercuric*, in which the valence is 2. The chlorides of mercury are the most useful compounds of this element.

*Mercurous chloride*,  $\text{Hg}_2\text{Cl}_2$ , is a white solid, quite insoluble in water. It is used in medicine as a liver stimulant under the name of *calomel*. When exposed to the light, this chloride forms mercuric chloride and metallic mercury. Calomel tablets that have been darkened by exposure to light should never be taken, *since mercuric chloride is extremely poisonous.*

*Mercuric chloride*,  $\text{HgCl}_2$ , forms beautiful white crystals. This chloride, which is commonly called the *bichloride of mercury* or *corrosive sublimate*, dissolves quite readily in water. One part of the salt to 1000 parts of water forms a good antiseptic solution, although other less poisonous disinfectants are known. Sometimes it is used medicinally, but the dose is  $\frac{1}{64}$  of a grain, and there are 7000 grains in an avoirdupois pound. *Bichloride of mercury tablets have no place in the family medicine cabinet.* The whites of raw eggs, or raw milk, may be used as an antidote for mercury poisoning, since the mercury combines with the albumin of the eggs or milk to form an insoluble compound.

★ *Mercuric oxide*,  $\text{HgO}$ , finds some use as red precipitate, and *mercuric sulfide*,  $\text{HgS}$ , may be sublimed to form a red



solid used as a pigment under the name *vermilion*. Mercury pigments have been used on the bottoms of ships to prevent fouling.

Nearly all compounds of mercury are antiseptic, but they are so heavy that they do not penetrate tissues readily. Dye-stuffs do penetrate tissues readily. Therefore the Medical School of Johns Hopkins University prepared *mercurochrome* by introducing mercury into the molecule of fluorescein, a dye-stuff of great penetrating power. This compound finds use as an antiseptic.

### SUMMARY

This family of elements includes *magnesium*, *zinc*, *cadmium*, and *mercury*. They range from the active metal magnesium to the inactive metal mercury. The group valence is 2, although mercury sometimes has a valence of 1.

Magnesium occurs in *dolomite*, *asbestos*, *talc*, and *carnallite*. It is extracted by electrolysis of *carnallite*, a double chloride.

*Magnesium* is an active silver-white metal. It burns with an intense white light. In moist air, it forms a protective coating of the basic carbonate. It finds use in fireworks, flashlight powders, and in making the alloy *magnalium*. The oxide, sulfate, and several natural silicates are important compounds of magnesium.

Zinc occurs in nature as the sulfide, the carbonate, and the oxide. It is extracted by roasting the ore and then heating the ore with a mixture of powdered coal.

*Zinc* is bluish white. It is self-protective; hence it forms a good coating for protecting iron, as in *galvanizing*. It interacts with acids easily. *Zinc oxide* is an important paint base. *Zinc chloride* is a wood preservative. *Brass*, *bronze*, and *German silver* are alloys of zinc.

*Mercury* occurs as the sulfide. It is extracted by roasting the ore. It is the only liquid metal. Mercury is inactive, but it is attacked by strong oxidizing acids, such as nitric and sulfuric.

Mercury finds use in the manufacture of scientific instruments. Its alloys are called *amalgams*.

Mercury forms two chlorides: *mercurous chloride*, or calomel; *mercuric chloride*, or corrosive sublimate. Mercuric sulfide is a red pigment known as vermilion.

## QUESTIONS

### GROUP A

1. Account for the explosive nature of flashlight powders.
2. Name two important alloys of zinc; of bismuth; of antimony. Of what is each one composed?
3. What is meant by a refractory? Give two or three examples.
4. Why should active poisons never be kept in medicine cabinets? What do you think of the idea that dangerous poisons be dispensed in irregularly shaped bottles?
5. Name three methods used to prevent the decay of wood.
6. What properties has mercury that makes it suitable for use in thermometers? In barometers?
7. What is meant by a heat insulator? Name as many places about the house as you can where heat insulators are desirable.
8. How would you treat a case of poisoning by a salt of mercury?
9. What is meant by the term "self-protective" as applied to a metal?

### GROUP B

10. Write the equation to represent the chemical action that occurs when a strip of zinc is immersed in a solution of copper nitrate; in a solution of mercuric nitrate.
11. Hydrogen sulfide turns white lead black. Why does it not discolor zinc?
12. Would you expect a solution of zinc chloride to give an acid or an alkaline reaction? Why is such a solution suitable for use in soldering?
13. What compound do you think would be formed by heating a mixture of mercuric chloride and mercury?

14. Give three methods of preparing zinc sulfate. Write the equations in each case.

15. Make a list of as many applications of the mineral asbestos as you can find.

16. Why is cadmium plating superior to galvanizing for certain purposes?

## PROBLEMS

## GROUP A

1. How many pounds of mercury can be obtained by roasting one ton of 85% mercuric sulfide?

2. How many pounds of zinc oxide can be made from 1500 lb. of zinc?

## GROUP B

3. How many pounds of cadmium sulfide can be precipitated by adding an excess of a soluble sulfide to 100 lb. of cadmium chloride?

4. How many liters of hydrogen sulfide will be needed to precipitate all the mercury from 1000 gm. of a 10% solution of mercuric chloride?

## CHAPTER 34

### THE ALUMINUM FAMILY

#### Vocabulary

**Tenacious.** Cohesive; not easily pulled apart.

**Mauve.** A purplish color.

**502. Introductory.** There are several elements in this family, but the only ones that have any great commercial importance are *boron* and *aluminum*. Boron is really an *acid-forming* element that resembles silicon to some extent in its chemical properties. Aluminum is generally considered a *base-forming* element, but its hydroxide may also ionize as an acid. Its hydroxide is *amphoteric*. Both elements have a valence of 3.

#### A. BORON

**503. Boron and Boric Acid.** In the alkaline desert regions of southern California and Nevada extensive beds of borax, or *sodium tetraborate*,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , are found. *Colemanite*, a calcium borate,  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ , is a more important boron mineral than borax. Several hundred tons of this mineral are mined daily in Death Valley, California, and treated with sodium carbonate to remove the calcium, and prepare borax. These beds, with some *ulexite*, a double salt of sodium and calcium borate, supply the boron needed for the boric acid and borax industries.

The element *boron* has been isolated, but it has no industrial applications. *Boric acid*,  $\text{H}_3\text{BO}_3$ , crystallizes in nearly colorless, lustrous scales. It occurs in nature in volcanic regions, especially in Tuscany, where it issues from the earth in steam jets. Boric acid is a weak acid that has antiseptic

properties. It is so weak that it may be introduced into the eye with safety. It finds use as an eye-wash and a mouth-wash. Boric acid imparts to a colorless flame a beautiful green color. *Norbide*, a carbide of boron having the

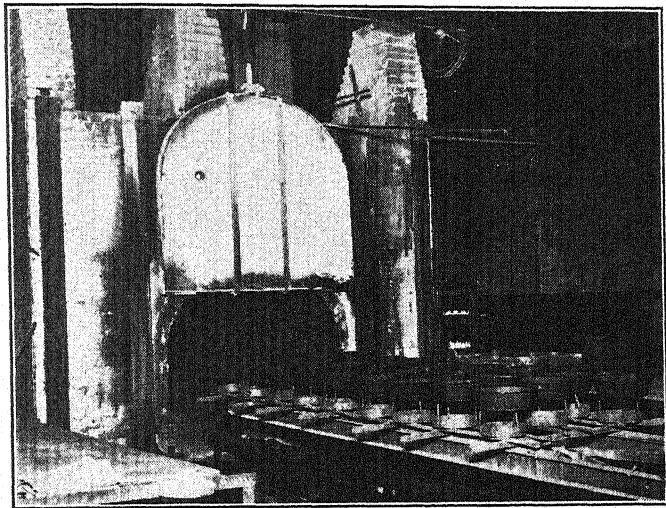


FIG. 287. — The mixture for enameling is fused, poured into cold water, and then powdered. The iron pan is dipped into a suspension of this powder in water and then heated in a furnace long enough to fuse the coating.

formula  $B_4C$ , is the hardest synthetic compound that has ever been made. It finds use as an abrasive.

**504. Borax, or Sodium Tetraborate,  $Na_2B_4O_7$ .** This is doubtless the best known of the boron compounds. Around the household, it is used to soften hard water. It finds some use as a mordant and as an antiseptic. It dissolves metallic oxides; hence, it is useful as a flux in soldering, and to provide a clean metallic surface for welding metals. The borates of certain metals are used for making glazes and enamels. Figure 287 shows some enamel ware that has just

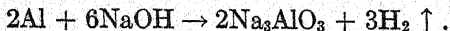
been removed from the furnace. We have already learned that pyrex glass is a boro-silicate glass.

**505. The Borax Bead Test.** If we make a small loop in the end of a platinum wire, dip it into powdered borax, and then heat it, the borax will first swell up to several times its former size, and then fuse to a clear, colorless glass-like bead. Such a bead may be heated with a small speck of some metal or metallic compound, such as cobalt nitrate,  $\text{Co}(\text{NO}_3)_2$ . In the oxidizing flame, the oxide of the metal is formed and it dissolves in the borax bead, imparting to it a color that depends upon the metal used. Cobalt produces a blue bead, nickel a brown bead, and chromium a green one. This *borax bead test* may be used to identify certain metals.

## B. ALUMINUM

**506. Properties of Aluminum.** Aluminum is a white metal, less than three times as dense as water. It is only one-third as dense as iron. Aluminum is ductile and malleable, but it is not so tenacious as brass, copper, or steel. It ranks with the best conductors of electricity; silver, copper, and gold are the only metals that surpass aluminum in this respect. Aluminum may be welded, cast, or spun, but it can be soldered only with difficulty, and by the use of a special solder.

Aluminum takes a high polish, but it soon becomes covered with a very thin coating of aluminum oxide. This gives the metal a slight bluish tint. The color of the oxide resembles that of the metal so much that many persons believe that aluminum does not tarnish at all. The oxide is adherent, and the metal is self-protective. Hydrochloric acid and hot sulfuric acid attack aluminum and form salts of the respective acids. Nitric acid hardly affects it at all. Salt water corrodes aluminum rapidly, and the strong bases interact with it, forming *sodium aluminate* and hydrogen. The equation follows:



**507. Uses of Aluminum.** To some extent aluminum is used instead of copper for electrical conductors. It is a poorer conductor than copper, but the wires can be made larger to reduce the resistance and yet the wire will be lighter than a copper wire that carries the same current. Thus the strain upon the support for the conductor is less. The aluminum flashlight bulbs are more convenient to use than flashlight powders, and the products of combustion cannot escape into the air to irritate the throats and lungs of persons in the room. Such bulbs contain aluminum foil, crumpled to give a large surface, and enough oxygen to oxidize the foil completely. The foil burns with an intensely white flame when ignited by the hot filament.

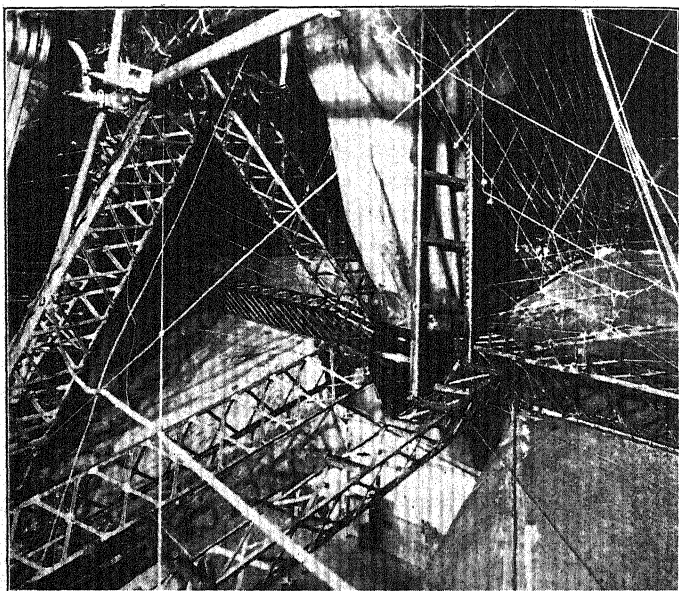
Powdered aluminum finds use as a paint; it serves to protect the surface of iron, as in the "silvering" of radiators. For wrapping food and candy, aluminum foil is being used to take the place of tin foil. Many small novelty articles are made of aluminum. For several reasons aluminum finds favor in the manufacture of cooking utensils of all kinds: (1) It is light and durable; (2) It is a good conductor of heat; (3) It is easily kept clean; (4) The tarnish is much the same color as the metal, and the salts of aluminum that may be formed in cooking acid fruits and vegetables are non-poisonous.

**508. Alloys of Aluminum.** *Duralumin* is an alloy of aluminum, copper, and manganese that is less than half as dense as steel and nearly as strong. It may contain a small per cent of magnesium. It finds extensive use in making the framework of dirigibles and airplanes and in other places where a strong, light alloy is needed. The framework of the *Los Angeles* is made of this alloy. (See Fig. 288.) *Magnalium* is an alloy of magnesium and aluminum that was mentioned under magnesium. There are several alloys of aluminum and copper known as *aluminum bronze*. The color varies with the relative percentages of the metals. One alloy resembles silver, and another one gold. They are hard and



elastic and take a high polish. Aluminum alloys are used for making airplane and automobile parts, and for various small articles.

**509. Aluminum Oxide,  $\text{Al}_2\text{O}_3$ .** *Corundum* and *emery* are natural oxides of aluminum. They find use as abrasives.



*Courtesy U.S. Navy*

FIG. 288. — A photograph of the interior duralumin framework of the *Los Angeles*.

Emery may be used in the form of emery paper, emery cloth, or grinding wheels. *Rubies* and *sapphires* are pure specimens of aluminum oxide colored by traces of metallic oxides. Many synthetic rubies and sapphires are now manufactured by fusing pure aluminum oxide and building up successive layers of the product as it solidifies. In making the clear sapphires, no coloring matter is added. To form

the blue color, titanium oxide is added. Rubies are colored by the addition of chromium. These gems are not imitations. They are identical in color and properties with the natural stones and cannot be distinguished from them. *Alundum* is an artificial oxide of aluminum made by fusing bauxite in an electric furnace. It finds use as an abrasive. (See

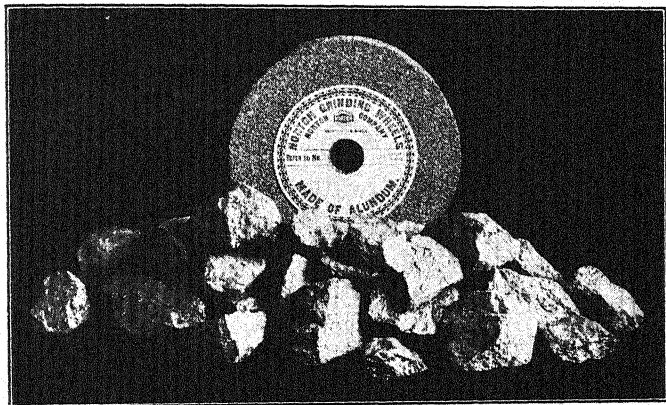
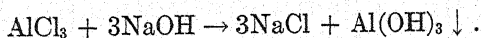


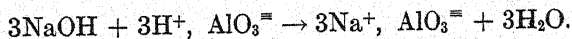
FIG. 289. — Alundum, a much used abrasive.

Fig. 289.) It is also used to make laboratory apparatus, such as crucibles, funnels, and tubing.

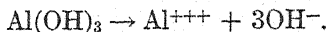
★ 510. **Aluminum Hydroxide,  $\text{Al}(\text{OH})_3$ .** This hydroxide is very interesting to the chemist, because it is able to act as either an acid or a base. If we add sodium hydroxide to a solution of some aluminum salt — aluminum chloride, for example — a white, gelatinous precipitate of aluminum hydroxide is first formed:



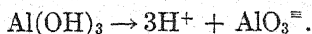
This precipitate is insoluble in water, but if we add an *excess* of sodium hydroxide, it forms sodium *aluminate*, which is soluble. The equation follows:



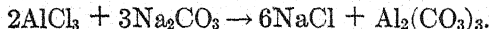
These reactions show the *amphoteric* nature of aluminum hydroxide. In the presence of any strong acid, aluminum hydroxide ionizes to slight extent as an extremely weak base:



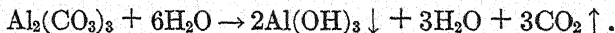
When it is treated with a very strong base in *excess*, it then ionizes as a very weak acid, and it interacts with the base to form aluminates, which may be considered salts of aluminic acid.



Aluminum hydroxide is such a weak base that its salts of weak acids are almost completely hydrolyzed. We would expect, for example, to have aluminum carbonate precipitated if we add sodium carbonate to a solution of aluminum chloride. The following equation represents what one might expect:

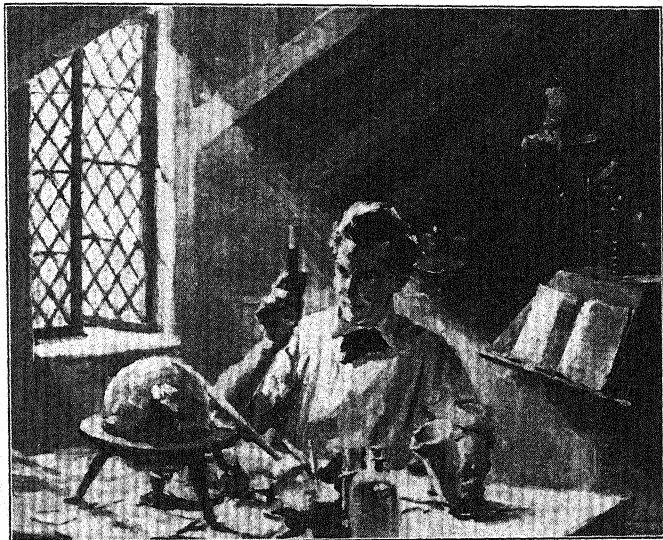


But we do not get what might be expected. If any aluminum carbonate is formed it immediately hydrolyzes and forms aluminum hydroxide, which is always precipitated if we add a *soluble carbonate*, or even a *soluble sulfide*, to a solution containing an aluminum salt. The equation follows:



In Chapter 8, which deals with water purification, we learned that aluminum hydroxide forms a bulky precipitate, which will adsorb bacteria and sediment in water and carry them down to the bottom of the reservoir as it settles. Aluminum hydroxide is useful as a *mordant* in the dye industry. The word mordant comes from the Latin word *mordere*, which means "to bite." A mordant seems to fasten itself to the fibers of the fabric to be dyed, and the dye unites in some way with the mordant, sometimes by

adsorption. Thus a mordant makes a dye *fast*. The aluminum hydroxide as a mordant is usually precipitated upon the fibers by hydrolysis before they are dipped into the dye bath. Colored pigments for use in paints are sometimes made by precipitating a dye of some kind with aluminum hydroxide. Such insoluble compounds are called *lakes*.



*Courtesy of Parke Davis & Co.*

Fig. 290. — William Henry Perkin (1838–1907) was an English chemist. He made the first aniline dye from coal tar, and became the founder of the synthetic dye industry.

Various dyes may be used, and different colors are also obtained by using the same dye with different mordants.

★ **511. Dyeing.** Formerly the chief source of dyes was from animal, plant, and mineral compounds. In 1856, a young Englishman, William Henry Perkin, succeeded in preparing *mauve* artificially by oxidizing aniline, a coal-tar product. This discovery marked the beginning of the synthetic dye industry. (See Fig. 290.) Now a great many dyes

are made synthetically from coal tar, a substance that before the above date was considered almost worthless.

A good dye should have a pleasing shade; it should not fade when exposed to the light; it should not be removed from the fabric by rubbing, washing, or perspiration; it should not weaken the fiber. Wool and silk are sometimes dyed directly, as these fibers combine with certain dyes without the use of a mordant.

Some *insoluble* dyes, such as indigo, are precipitated on the fiber. Indigo is now prepared artificially. In the presence of a reducing agent it forms indigo white, a compound soluble in alkalis. When textile fibers are saturated with a solution of indigo white and then exposed to the air, oxidation occurs, resulting in the formation of the insoluble indigo blue. This dye is extensively used in dyeing blue serge. The color is very fast.

*Acid dyes*, which consist of alkali or calcium salts of color acids, are used in acid solution. They are not used for dyeing cotton and linen, but they dye silk and wool directly. Acid dyes are very fast to light, but they cannot be washed with a soap or powder containing any free alkali, since a base causes the acid dye to dissolve rapidly.

On the other hand, *basic dyes* fade quite rapidly when exposed to the light, but they are not removed by washing. They dye wool and silk directly, but when used with cotton or linen, a mordant is required. Such dyes as methyl violet, methylene blue, malachite green, fuchsine, etc., are examples of basic dyes.

To secure good results in dyeing, the fabric must be thoroughly cleansed, and it should be wet when introduced into the dye bath; the dye should be kept slowly boiling; and the goods should be agitated so all parts will be dyed uniformly. In dyeing cotton goods, the addition of such salts as sodium chloride, or sodium sulfate, makes the dye less soluble and causes more of it to unite with the fabric. This

"salting out" process is a good illustration of the common ion effect. (See Section 301.)

After Perkin had started the synthetic dye industry, further problems pertaining to the industry were worked out, largely in Germany. By 1914 Germany had a near-monopoly upon the dye industry. Of several thousand dyes that had been made in Germany by synthesis, nearly one thousand were being marketed at that time. The value of the dyes themselves was not so great compared with that of the products of many other industries. But dyes are also valuable because they increase the value of other products. The total value of the dye in a necktie is not very great, but the fact that it is there makes the necktie much more valuable than it would be otherwise. At the beginning of the World War, there were only six or seven concerns in the United States making any dyes at all. Dyes soon became scarce and many of them were unsatisfactory because some jobbers sold their stocks of cheap dyes to hosiery manufacturers, where the best dyes are needed. Some unscrupulous jobbers diluted their pre-war stocks of dyes with as high as 99% of salt. The chemists in America attacked with vigor the problem of building up a dye industry. By the end of the war there were more than ten times as many dye factories in the United States as there were in 1914. Now a large part of the demand for dyes is taken care of by home manufacture, and the dyes are satisfactory.

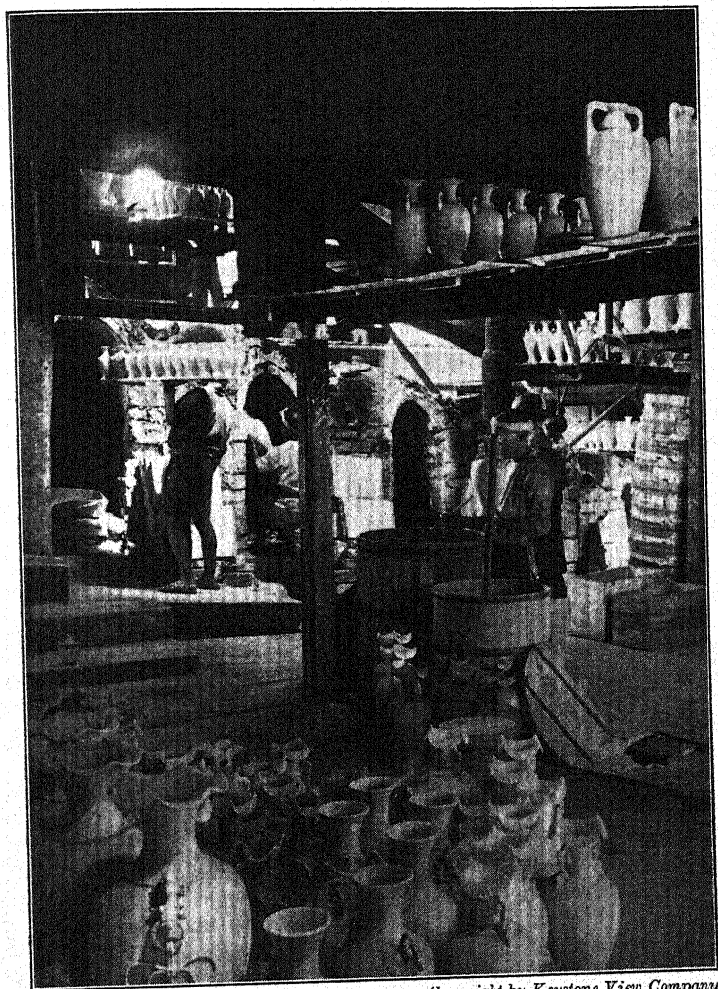
**512. Alums.** If we mix solutions of potassium sulfate and aluminum sulfate and then evaporate the mixture, a *double salt* separates as crystals. The formula of this alum is  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ . Any double sulfate formed in the same manner and having similar properties is called an *alum*. Instead of potassium sulfate, either sodium or ammonium sulfate is often used. Such trivalent metals as iron and chromium may take the place of the aluminum. The

general formula,  $M'_2M'''_2(SO_4)_4 \cdot 24H_2O$ , is used to represent alums, in which  $M'$  is some univalent element, or group, and  $M'''$  a trivalent metal. Alums are used as mordants. *Aluminum sulfate*,  $Al_2(SO_4)_3$ , is used largely instead of alum for water purification and as a mordant.

**513. Silicates of Aluminum.** *Fuller's earth* is a silicate of aluminum used for cleaning fabrics and for clarifying oils. *Ordinary mica* is a potassium aluminum silicate. It is translucent and infusible. Under the *incorrect* name of "isinglass" it is used in stoves. As an insulator mica is used in making commutators for dynamos and motors. The *feldspars* are complex silicates, usually containing aluminum silicate with either sodium or potassium silicate. By the action of water and carbon dioxide, disintegration or weathering occurs and the alkalis are leached out as soluble silicates or carbonates. We have left a *white clay*, or hydrated aluminum silicate, known as *kaolin*. The colored clays found in soils usually contain iron and sometimes calcium, the color being largely due to iron compounds. *Ultramarine* is a complex substance made by heating together clay, soda, and sulfur. It is found in nature as the mineral *lapis lazuli*. The artificial product is a more highly colored pigment; it is used also as a laundry blue, and to neutralize the yellow tint of wood pulp, and linen fibers.

**514. Applications of Clays.** Clay becomes plastic when it is mixed with water, and it can be molded into any desired shape. When the plastic mass is dried and baked at a high temperature it does not melt but it contracts and forms a hard, porous mass capable of resisting pressure. This property of clay makes it suitable for use in making *brick*, *earthenware*, and *porcelain*. In making bricks an impure clay is used. The red color is due to the presence of iron compounds. In making *vitriified brick* a high enough temperature is used to start fusion, thus filling the pores at the surface. *Fire bricks* are made of clay and sand. *Earth-*





*Copyright by Keystone View Company*

FIG. 291. — Kilns in which the famous Satsuma pottery is fired.

*enware* and *tile* are made from coarse clays and a low temperature is used in "firing," so the mass remains porous. Flowerpots are examples of this ware. When such clays are heated to a higher temperature they are vitrified throughout the mass, forming *stoneware*. The cheaper kinds of stoneware are glazed by throwing salt into the furnace. *Porcelain* or *china* is made from a very pure white clay mixed with powdered feldspar. It is usually fired twice. After the first firing the porous biscuit is dipped into water containing in suspension a mixture of powdered feldspar and kaolin. During the second firing the feldspar melts and fills the pores so that the china becomes impervious to liquids. (See Fig. 291.) New Jersey and Ohio produce enormous quantities of pottery. Trenton, New Jersey, and East Liverpool, Ohio, are the leading cities in the pottery industry. Some very fine white clays are found in France, Czechoslovakia, and Japan. Large quantities of high-grade porcelain and china are imported from those countries.

### SUMMARY

*Boric acid* and *borax* are the most important compounds of boron. Both find use as antiseptics. Borax is also used in soldering and welding to dissolve the tarnish and give a clean surface, and in the manufacture of glass and enamels.

*Aluminum* is a light, white metal. It is a good conductor of heat and electricity. It is self-protective. Aluminum is used for paint, to purify steel, for electrical conductors, and in making cooking utensils. Alloys of aluminum and copper are known as aluminum bronze. Duralumin is now used to make the framework of dirigibles and for other purposes where a light, strong alloy is needed.

Natural and synthetic *rubies* and *sapphires* consist of aluminum oxide. Impure *aluminum oxide*, or *emery*, is used as an abrasive. *Alundum* is a manufactured oxide of aluminum.

*Aluminum hydroxide* is *amphoteric*; it may act as an acid or as

a base. It is used in water purification and as a mordant. *Alums* are double sulfates of aluminum that find use as mordants.

*Mica, clay, and fuller's earth* are silicates of aluminum. Clay is used in making brick, tile, earthenware, stoneware, and porcelain.

QUESTIONS

GROUP A

1. Why is it not desirable to scour aluminum cooking utensils frequently?

2. State the advantages aluminum has for use in making cooking utensils. If it has any disadvantages, name them.

3. What application is made of the fact that carbon dioxide is liberated when such a compound as aluminum sulfate comes into contact with sodium bi-carbonate?

4. What objection is there to the use of washing soda or alkaline scouring powders in cleaning aluminum?

5. What is an abrasive? Name several that we have studied.

6. How is aluminum used as a reducing agent? For making flashlights?

7. Since clay contains aluminum and it is much more abundant than bauxite, why not use the former for obtaining aluminum?

8. Explain why so large a percentage of the aluminum produced is used in the automobile and airplane industries.

9. Why should you expect a pawnbroker to hesitate about lending money on a ruby or sapphire?

10. At one time boric acid and borax were used as food preservatives. Why have they fallen into disuse for such a purpose?

GROUP B

11. What is a lake? What are the purposes of a mordant?

12. What elements have we studied whose hydroxides act either as acid-formers or base-formers? In what groups in the periodic table are such elements found?

13. Under what conditions does an amphoteric hydroxide act as a base? As an acid?

14. Why do we have aluminum hydroxide precipitated and not aluminum carbonate when we add sodium carbonate to a solution of an aluminum salt?

15. Write the equation to show what action occurs when sodium sulfide is added to a solution of aluminum chloride.

16. In mordanting, the cloth is sometimes soaked in aluminum acetate solution and then treated with steam. What compound do you think is precipitated by this method? Explain.

17. How does the colloidal nature of aluminum hydroxide make it useful in the dye industry?

18. What are the characteristics of a satisfactory dye-stuff?

## PROBLEMS

### GROUP A

1. What per cent of borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ , is boron?
2. How many pounds of sodium hydroxide are needed to dissolve 10 pounds of aluminum? (See equation on page 564.)

### GROUP B

3. How many liters of hydrogen are set free when 50 gm. of aluminum are treated with 100 gm. of sodium hydroxide?

4. How many grams of aluminum will remain after the reaction of Problem 3 is complete?

## SUPPLEMENTARY PROJECTS

Prepare a report on one of the following topics:

1. Coal-tar colors.

References: SLOSSON, E. E., *Creative Chemistry*, Chapter IV. Chemical Foundation, Inc.

HOWE, H. E., *Chemistry in Industry*, Volume II, Chapter IV. Chemical Foundation, Inc.

2. How porcelain is made.

Reference: HOWE, H. E., *Chemistry in Industry*, Volume II, Chapter VI. Chemical Foundation, Inc.

3. Making gems artificially.

Reference: *Collier's*, 81:14, January 21, 1928.

## CHAPTER 35 ★

### SOILS AND FERTILIZERS

#### Vocabulary

**Residual.** Soil remaining where it was originally formed by weathering.

**Humus.** The organic portion of the soil, formed by the partial decomposition of vegetable or animal matter.

**Potash.** A name given to compounds of potassium.

**Feldspar.** A natural silicate of aluminum with such other elements as sodium, potassium, calcium, etc.

**Marl.** An earthy deposit, consisting largely of clay and limestone, which is used as a fertilizer.

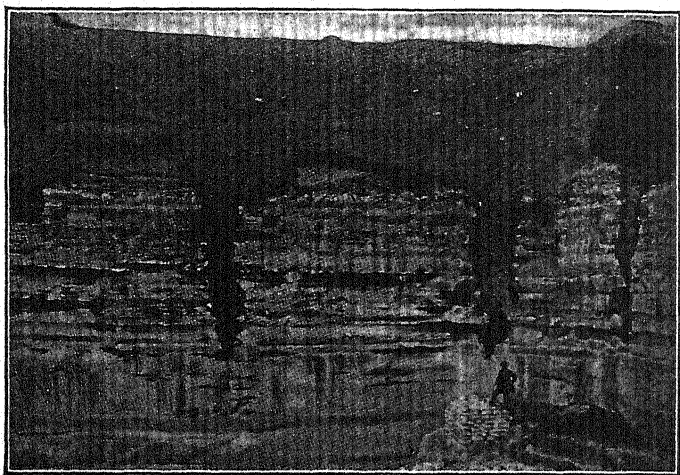
#### A. SOILS

**515. Bed Rock, the Source of Soils.** The bulk of the earth's crust is made up of solid rock, or what is commonly called *bed rock*. In most localities the bed rock is covered with a layer of soil that may vary in depth from only a few inches to a hundred feet or more. New soil is slowly being formed by a process known as *weathering*. Such agents as oxygen, carbon dioxide, water, and other substances are constantly acting upon bed rock and converting it into *manile rock*, or soil. (See Fig. 292.) Plants and animals, wind, and alternate freezing and thawing all act as agents in breaking up large masses of solid rock into smaller fragments.

Soils formed by weathering may remain just where they were formed. Such soils are called *residual soils*. Sometimes soils are transported by various agencies, such as wind, running water, and glaciers, to a different locality from that in which they were formed. Much of the deep, fertile soil of the Middle West was brought from Canada by the great glaciers during the prehistoric period when the northern

part of North America was covered by a huge sheet of ice. Running water often carries the finest, most fertile, soil downstream from one farm to another where it is deposited; or it may carry such material into the ocean where it is dispersed.

**516. Kinds of Soil.** The nature of a soil depends upon the constituents of the rock from which it was formed. When



*Salisbury's Physiography, by permission*

FIG. 292. — An illustration showing the irregular contact of solid rock below, with soil, subsoil, etc., above. The rock has decayed so that the subsoil extends down irregularly into it.

sandstone weathers, a *sandy* soil is formed; the disintegration of limestone forms a *limy* soil; *clay* soils are formed by the weathering of shale, slate, feldspar, and granite. Granite is a mixed rock; when the quartz it contains weathers, sand is the product formed; when the mica and feldspar weather, clay is produced. A transported soil is quite apt to be a mixed soil since the transporting agent may bring from different sources the materials of which it is composed. A mixture of sand and clay is called *loam*. If the amount of clay is rela-

tively large, it is called a *clay loam*; if it is small in proportion to the amount of sand, the soil is a *sandy loam*. The decomposition of organic matter in the soil forms *humus*. When the decay of organic matter is quite rapid, on account of its being exposed first to the air and then to water, *muck* is formed. It is soft and spongy, and has usually lost all resemblance to the organic matter from which it was formed.

**517. Elements Needed by Plants.** The elements absolutely needed by plants include *carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, sulfur, calcium, iron, and magnesium*. *Chlorine, silicon, and sodium* are essential to the *full* development of certain plants. Carbon is obtained from the carbon dioxide of the air; oxygen from the air and soil water; and hydrogen from the soil water that enters the plant through its roots. The other elements must be obtained from the soil. Since the compounds that contain these elements are usually solids, they cannot be absorbed by the roots of the plant unless they dissolve readily in the soil water. Recent experiments show that *manganese* produces a decided effect upon the growth of plants. It appears to act as a stimulant in some cases, and in others as a real plant food. Aluminum, too, seems to be beneficial to some plants.

**518. Fertility of Soils.** A fertile soil contains all the elements needed for the proper development of plants. These elements, too, must be in *available* form. In other words, they must be capable of dissolving in water so they can be taken up by the roots of the plant. A poor soil is deficient in one or more important constituents needed for plant growth. A soil may lose its fertility: (1) By the continual removal of the essential elements required by plants during the successive harvesting of crops; (2) By the leaching out of the soluble matter by rain water; (3) By burning out the *humus* by excessive use of lime or by alkalis present in the soil. A loam that contains *humus* is generally a fertile



soil. The humus increases the capacity of a soil for holding water. It makes a clay soil more easily worked, and keeps its small particles from coalescing to form large aggregates. It also supplies nitrogen that is needed by the growing plant.

A soil may contain all the elements needed for plant growth, and yet not be fertile. The *colloidal* nature of a soil affects its fertility, since its ability to adsorb water and mineral salts depends upon the size of the particles present. In many cases the water stands on a piece of ground and causes the soil to become *sour* or *acid*. Throughout the Middle West much underground drainage is needed. Porous tile laid beneath the reach of the frost are extensively used in flat sections to carry off the excess water rather rapidly. On the other hand, the rainfall in some regions is so scanty that irrigation must be used to grow crops successfully.

Nearly all soils contain sufficient silicon, iron, magnesium, sodium, chlorine, calcium, and sulfur to supply the needs of plants. For the growth of certain plants that require a large amount of sulfur and calcium, such as onions, garlic, cabbage, etc., the addition of a compound containing these elements is necessary. *Calcium sulfate*, often called land plaster, is the compound generally used. Most soils also contain *nitrogen*, *phosphorus*, and *potassium*, but these elements are taken from the soil more rapidly by plants, and they must be replaced to keep the soil fertile. A sandy soil is likely to be deficient in potassium; soluble matter, or available mineral matter, may quite easily be leached out of such a soil. In fact, the rain water carries away to the ocean more valuable mineral matter every year from a soil than the plants can possibly remove. In a clay soil, potassium is practically always present, since *clay is a potassium aluminum silicate*. Feldspar contains potassium, and granite rocks generally contain considerable calcium phosphate. Thus the weathering of granite and feldspar supplies potassium and possibly phosphorus for plant use. Limestone

often contains fossils that furnish a soil with phosphorus from the bones of animals.

## B. FERTILIZERS

519. **Partial and Complete Fertilizers.** The decay of plant and animal matter produces natural fertilizers for the soil. But when crops are removed from the soil year after year, the natural fertilizers that find their way back to the soil are not sufficient in quantity to replenish the materials taken from the soil. Then commercial fertilizers should be used. Before a farmer can tell just what fertilizers a soil needs, an accurate analysis of the soil must be made by a

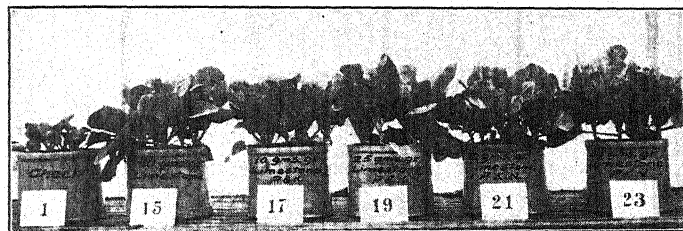


FIG. 293. — Effect of calcium carbonate in neutralizing the acidity of a muck soil, thus making the nitrogen available.

chemist. But the farmer can, by a systematic application of fertilizers for a period of several years, learn what elements his soil needs most. If his soil contains clay, he does not need to add much, if any, potassium.

Soils are classed as *acid*, *alkaline*, or *neutral*. Litmus may be used to determine the acidity of the soil, or its alkalinity. Acid soils are not suitable for the growth of certain plants, especially clovers, legumes, and certain root-crops. The acidity of a soil may be corrected by the addition of *slaked lime*, *marl*, or *powdered limestone*. Air-slaked lime is better than freshly hydrated lime, since it is not so caustic, and not so likely to injure vegetation. A muck soil is likely to be acid and to need *liming*. Figure 293 shows the effect of neutral-

izing a very acid muck soil with powdered limestone, and thus making available the nitrogen fertilizers in the soil. Care must be taken to avoid excessive or too frequent use of lime, since it may destroy the humus. Then the soil loses its fertility by having the nitrogen compounds destroyed. It also loses its ability to hold moisture. There is an old German proverb: "Lime makes a rich father, but a poor son."

A *complete* fertilizer contains some compound of *potassium*, some compound of *nitrogen*, and some compound of *phosphorus*. The elements themselves are not used, but always some soluble compound that contains the element. The compounds that are used vary a great deal, and some are richer in the essential elements than others. Hence the law requires that the analysis of a fertilizer shall be printed on the bag or container.

**520. How an Analysis Is Interpreted.** Since the nitrogen in a commercial fertilizer may be present as sodium nitrate, ammonium sulfate, or any one of a half dozen compounds, the nitrogen content of a fertilizer is often stated as "equivalent to ammonia." For example, if a manufacturer uses 100 lb. of ammonium sulfate in making 2000 lb. of fertilizer, the product contains 5% of ammonium sulfate. But approximately 25% of ammonium sulfate is ammonia. Hence the fertilizer will contain 25% of 5%, or 1.25% of ammonia, or we may say that it is "equivalent to 1.25% of ammonia." One per cent of sodium nitrate is "equivalent to 0.2% ammonia." Only 82% of ammonia is nitrogen. The farmer should not be misled by an analysis that shows per cent of nitrogen and "equivalent of ammonia," as they often do. (See Fig. 294.) He is not getting ammonia and nitrogen, but the nitrogen is present in the ammonia.

Potassium, or potash, is calculated as "equivalent to potassium oxide,  $K_2O$ ." One per cent of potassium sulfate, for example, is equivalent to 0.63% of  $K_2O$ . That means that

100 lb. of potassium sulfate would make 63 lb. of potassium oxide. Potassium chloride is richer in potassium, since 100 lb. of it would make 74 lb. of potassium oxide. They are not converted into potassium oxide at all.

In the case of phosphorus, the analysis tells us the total amount of phosphoric acid that could be made from the phosphorus compounds present. But the phosphorus may be present as secondary calcium phosphate, which is listed as "soluble phosphoric acid," or "available phosphoric acid"; it may be present as tri-calcium phosphate, which is listed as "insoluble phosphoric acid"; or it may be present as "reverted phosphoric acid." (See Section 382.) There is considerable overlapping in the analysis of fertilizers with respect to the content of phosphoric acid, and the total amount is seldom equal to the sum of the separate forms as shown by the analysis.

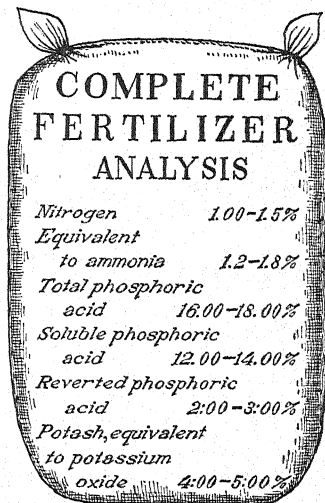


FIG. 294. — Illustrating the methods of indicating fertilizer analyses.

### C. NITROGEN FERTILIZERS

**521. Nitrogen Fertilizers.** Many of the sources of nitrogen for use as a fertilizer were mentioned when we studied nitrogen. (See Section 178.) Stable manure is rich in nitrogen. All decaying animal and vegetable matter contains nitrogen. Such products as tankage, fish scrap, slaughter house refuse, dried blood, and guano are extensively used in making commercial fertilizers. Sodium nitrate from Chile

is sold as a fertilizer. It is very soluble in water, and for that reason it is apt to be leached from the soils more quickly than some other nitrogen fertilizers. This defect may be partially overcome by using successive applications of the nitrate. *Calcium nitrate* is used as a fertilizer. It contains a slightly higher per cent of nitrogen than sodium nitrate.



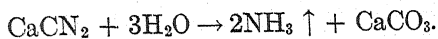
FIG. 295. — Effects of sodium nitrate upon the yield of wheat per acre.

Figure 295 shows how the addition of sodium nitrate to the soil increased the yield of wheat per acre.

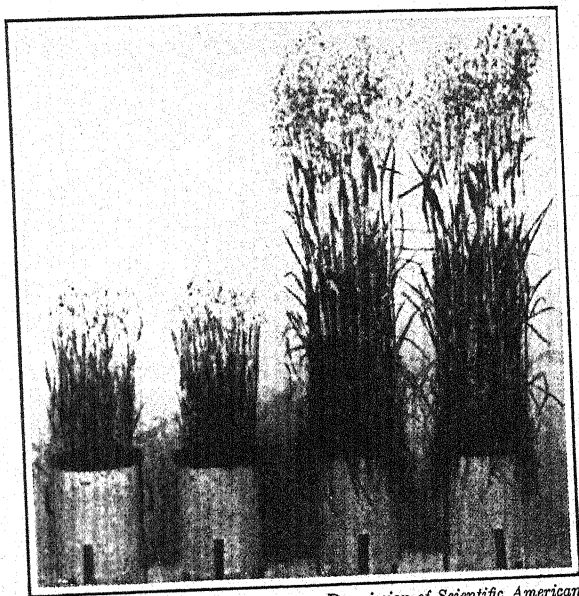
*Ammonium sulfate* is a by-product obtained in making coal gas. It contains 21% of nitrogen, and it is readily soluble. It is a good fertilizer, but it tends to make the soil acid.

*Calcium cyanamide*,  $\text{CaCN}_2$ , is a nitrogen compound that finds some use as a fertilizer. It is not so soluble as the nitrates mentioned, or as ammonium sulfate. In the soil it undergoes changes which convert it into ammonium com-

pounds. (See Fig. 296.) In some cases it has proved satisfactory, but in some others it has not been so successful. Hence it is often converted into ammonia by treatment with superheated steam. The equation follows:



Just prior to the dawn of the twentieth century Sir William Crookes predicted a world wheat famine. The nitrate beds



*Permission of Scientific American*

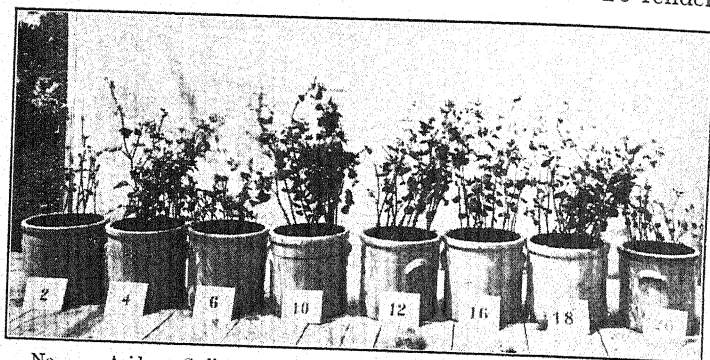
FIG. 296. — Oats grown with and without calcium cyanamide as a fertilizer.

in Chile appeared to be nearing exhaustion and the guano beds were being used up rapidly. But he did not know that in less than twenty years men would be taking nitrogen out of the air and making hundreds of thousands of tons of nitrogen fertilizers annually. We are glad to know that his prediction

proved to be incorrect, for the supply of nitrogen compounds that can be obtained by tapping the air is limitless.

#### D. PHOSPHORUS FERTILIZERS

**522. What Are the Sources of Phosphorus Fertilizers?**  
When we studied the element phosphorus, we learned that there are rich deposits of calcium phosphate in some of our eastern states, and that some of the western states also have rich deposits that have as yet been untouched. To render



No. Phos.	Acid Phos.	Sodium Phos.	Slag	Slag	Rock Phos.	Double Super Phos.	No. Phos.
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FIG. 297. — Effect of various phosphates on the growth of buckwheat.

these rock phosphates soluble, they are treated with sulfuric acid.

The bones of slaughtered animals are ground and made into fertilizers. They supply both nitrogen and phosphorus. The principal mineral matter in bones is calcium phosphate. They are sometimes acid-treated to make them more soluble. Both fish scrap and guano contain phosphorus that is of value as a fertilizer.

The phosphorus that is present in iron ores is removed in the slag when the iron is made into steel. This phosphate slag is a valuable source of phosphorus for use in fertilizers. Figure 297 shows the effect of various phosphates on the



growth of buckwheat. The acid phosphate, the superphosphate, and the slag are more soluble; hence they are of more value for immediate use. The rock phosphate shows only a little more than half the increase over the check that the acid phosphate does.

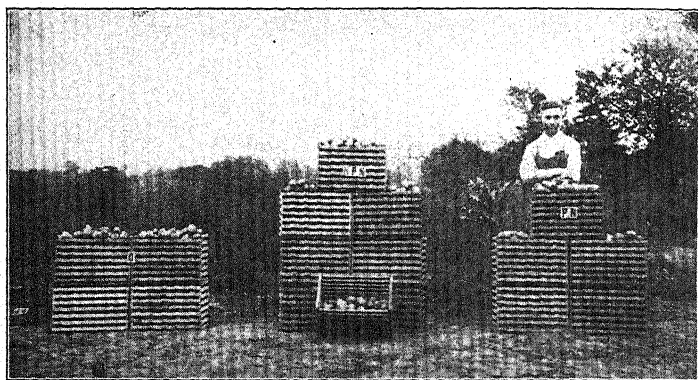
### E. POTASSIUM FERTILIZERS

#### 523. What Are the Sources of Potassium Fertilizers?

Although the United States exports large quantities of phosphate rock, compounds of potassium must be imported to meet our needs. The most abundant supply of potassium is found at Stassfurt, Germany. There are similar deposits in Alsace, which was a part of Germany prior to the World War. Both the chloride and the sulfate of potassium occur in the mineral deposits of these localities. The chloride of potassium contains slightly more than 52% of potassium, and the sulfate a little less than 45%.

In 1914, potassium compounds were being imported from Germany at a price of about \$40 per ton. Within a few months the price jumped to \$500 per ton, and it soon became almost impossible to buy any potassium compounds at all. We have seen how our glass manufacturers made glass without potassium. But no one has found a substitute for potassium compounds for plant use. Usually sodium compounds can be made to take the place of potassium compounds, but plants demand the potassium, and no substitutes. (See Fig. 298.) Hence it became imperative to make a more thorough search for potassium compounds in the United States. There are many sources, since potassium compounds are widely distributed, but no one source yields large amounts. For example, wood ashes contain potassium carbonate. Some potash is obtained from the scourings of wool, from plant refuse, from the waste products obtained during the manufacture of sugar and molasses, and from giant kelps or seaweeds which are dragged ashore along the Pacific Coast

and burned for their potassium compounds. Beds of potash were found in some dried lake regions of Nebraska, and they are now worked for their potash and for the borax they yield as a by-product. The deposits of potash found in Searles Lake, California, are more extensive. Rich beds of potassium compounds similar in nature and extent to the deposits found near Stassfurt have been discovered in the state of Texas. The *greensands* of New Jersey contain *glauconite*, a



*Courtesy N. V. Potash Export My., Inc.*

FIG. 298. — The potatoes in the boxes at the left were grown without added fertilizer. Those at the right were grown with phosphorus and nitrogen as fertilizers. The potatoes in the center boxes were grown with a complete fertilizer.

mineral that contains a silicate of iron and potassium. One of the problems yet to be solved is that of extracting the potassium from these deposits at a price low enough to compete with the imported products.

Feldspar rocks contain an abundant reserve supply of potassium, but they weather so slowly that they do not help to meet the demands for potash. No commercial method has yet been devised for making the potassium in feldspar available for immediate use. Some cement manufacturers do, however, use a potassium feldspar in making cement. By

the use of Cottrell precipitators some potash can be recovered from the stacks as a by-product. Since the cession of Alsace to France, the German monopoly of potash is broken. France and Germany have agreed, however, upon a common price that is but slightly lower than the price charged in 1914.

## SUMMARY

The process of changing *bed rock* into *mantle rock*, or soil, is known as *weathering*. If the soil remains where it was formed it is called *residual soil*.

Soils are known as *sandy*, *limy*, or *clay*, depending upon the nature of the rock from which they are formed. *Loam* is a mixture of sand and clay. Decaying vegetable matter in the soil forms *humus*.

Plants need hydrogen, oxygen, carbon, nitrogen, potassium, phosphorus, sulfur, magnesium, calcium, iron, sodium, chlorine, and silicon for growth. The first three are obtained from water and the air; the last three are less important and are generally present in all soils.

A fertile soil contains all the above elements in a form that makes them available for plant use. It should not be acid. Lime and powdered limestone are valuable for neutralizing the acidity of soils.

The elements that are likely to be lacking in a soil are *nitrogen*, *potassium*, and *phosphorus*. These may be added from time to time in the form of soluble compounds of these elements. They are called *commercial fertilizers*.

The *sources of nitrogen* include plant and animal refuse, sodium nitrate, calcium nitrate, ammonium sulfate, and calcium cyanamide. Many tons of nitrogen are now taken from the air annually to manufacture nitrogen compounds for plant use.

*Phosphorus* for use in making fertilizers is obtained from rock phosphates, from ground bone, from phosphate slag, guano, and fish scrap. The United States exports phosphate rock.

*Potassium compounds* are found in seaweeds, wood ashes, in the greensands of New Jersey, and in feldspar rocks. Fairly extensive beds have been found in Nebraska, Wyoming, and California.

Rich deposits are reported as having been found in Texas. The richest known beds of potassium compounds are found at Stassfurt, Germany, and in Alsace, France.

### QUESTIONS

1. How does the amount of rainfall affect the fertility of the soil?
2. Why is the soil of river bottoms so fertile? Recall the effect of the overflow of the Nile upon the fertility of the soil in Egypt.
3. How does the nature of the subsoil affect the ability of a soil to retain mineral matter to be used as plant food?
4. Why does letting a soil lie idle during the summer (summer fallow) improve its fertility?
5. Why is a loam generally a fertile soil? Would you expect a loam to be easily tilled?
6. What danger arises from too frequent addition of lime to soils?
7. What do you understand by a complete fertilizer?
8. Why is sulfuric acid used so extensively in the fertilizer industry?
9. Is powdered limestone suitable for liming soils? Is it suitable to use air-slaked lime?
10. Name as many crops as you can that may be used to enrich the soil.
11. The Indians in New England are said to have taught the early settlers to put a dead fish in each hill when planting potatoes. Would such practice be effective?
12. How are bacteria useful in enriching soils?

### SUPPLEMENTARY PROJECT

Prepare a report on the following topic:

1. Frauds in fertilizers.

Reference: CHAMBERLAIN, J. C., and BROWNE, C. A., *Chemistry in Agriculture*, Chapter XVI. Chemical Foundation, Inc.

## CHAPTER 36

### THE IRON FAMILY

#### Vocabulary

**Tempered.** Heat treated to give the desired hardness and toughness.

**Entrained.** Incorporated within the mass during the rolling process.

**Trunnion.** Either of two opposite pivots extending from the side of a converter.

**Pyrometer.** An instrument for measuring temperatures higher than the upper limit of the thermometer.

**524. Introductory.** If we refer to the periodic table, we find three elements in Group 8 that resemble one another in many ways. The elements are *iron*, *nickel*, and *cobalt*. In their valences, and in the manner in which they form compounds, these three elements are alike. The elements have a valence of 2 in their "ous" compounds, and a valence of 3 in their "ic" compounds. *Pure* iron is almost unknown in industry. Traces of other substances change its properties decidedly. Hence we find *cast iron* and *steel* used very extensively, because they contain small quantities of other elements that impart to the iron unusual properties. The United States produces about 40,000,000 tons of steel annually.

#### A. IRON AND STEEL

**525. How Iron Is Found in Nature.** There are many minerals found in nature that contain iron. Nearly all soils contain some iron compounds. There are four important ores of iron. *Hematite*,  $\text{Fe}_2\text{O}_3$ , is the most abundant. *Magnetite*,  $\text{Fe}_3\text{O}_4$ , and *limonite*, a hydrated oxide of iron, are important ores. *Siderite*, a carbonate of iron, is also used

as a source of iron. Several sulfides of iron are found in nature, but they are not used as ores, because it is difficult to free the iron from the sulfur, which makes steel brittle. Iron ore is mined in Minnesota, Michigan, Alabama, Pennsylvania, Ohio, and West Virginia. Iron is found in the red blood cells, where it plays an important part in the life process.

**526. How Iron Is Mined.** When the iron ore is found near the surface, as it is in northern Minnesota, open pit

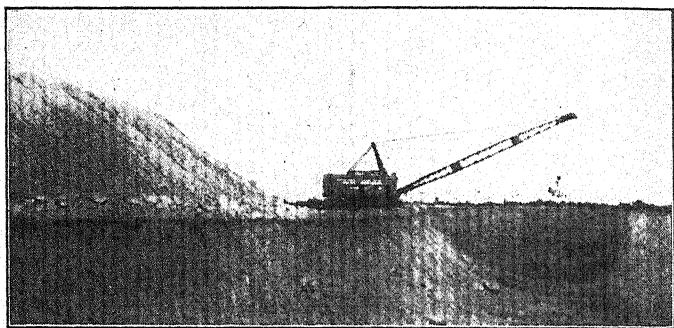


FIG. 299. — Steam shovel used for "stripping" ores in Northern Minnesota.

mining is used. The method is not unlike that of quarrying. If the ore is covered with loose, earthy material, steam shovels may be used to remove the surface layers "to get at the ore underneath." In some parts of Minnesota, as much as 200 feet of such material is stripped off. (See Fig. 299.) The ore is loose enough so it may be loaded on cars by means of steam shovels, and no hand labor is necessary. No other place has been found where iron ore can be mined so cheaply.

In northern Michigan, shaft mining is used. The mines vary from 400 ft. in depth to about 2000 ft. The ore is loose, and the mines must be timbered to prevent the ore from falling upon the miners. The iron ore is loaded into small

cars which are hauled to the mine shaft and hoisted by means of cables. (See Fig. 300.)

**527. The Composition, Properties, and Uses of Cast Iron.** In Chapter 30 we learned how iron is extracted from its ores. As the iron comes from the blast furnace, it contains

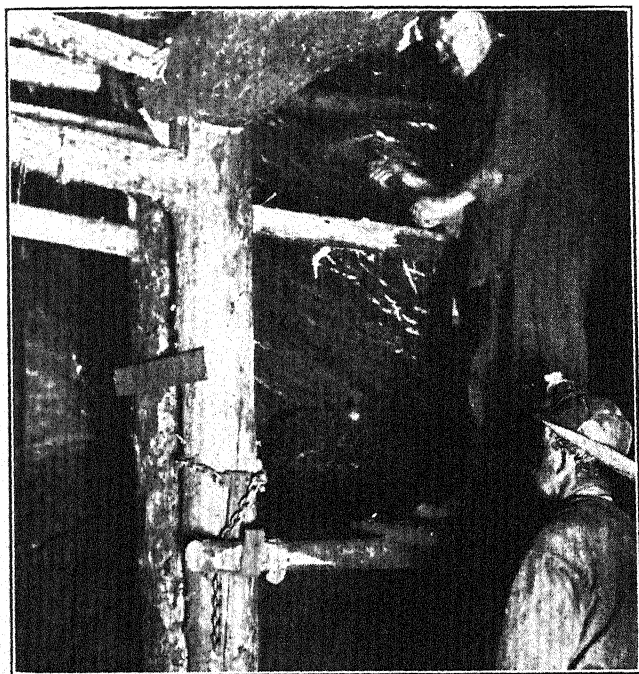


FIG. 300. — Underground or shaft mining. The loose ore must be heavily timbered.

considerable carbon and other impurities. It is known as *pig iron* or *cast iron*.

*Cast iron* contains from 2% to 5%, or slightly more, of carbon, which may exist as free carbon in the form of graphite, or it may be combined with the iron in the compound iron carbide,  $\text{Fe}_3\text{C}$ . This compound, which is called *cemen-*



*tite*, is extremely hard. The amount of carbon present in the form of cementite depends upon the rate at which the cast iron is cooled. If cooled quickly, very little of the iron carbide will decompose into iron and graphite. Such cast iron is very hard, and it is white in color. Hence it is known as *white cast iron*. If the cast iron is cooled slowly, it will contain more graphite. The product, which is known as *gray cast iron*, is softer and it is gray in color. The other impurities found in cast iron are *phosphorus*, *sulfur*, *silicon*, and *manganese*.

Cast iron is hard, crystalline, and brittle. It is neither malleable nor ductile. It cannot be welded directly, because it has a sharp melting point. Cast iron cannot be tempered. Its melting point depends upon the per cent of carbon present, but it is usually from  $1100^{\circ}$  to  $1200^{\circ}$  C. It is not very tenacious, but it can sustain very great weights without being crushed by them.

As the name implies, this form is suitable for making castings. The molten iron is poured into sand-lined molds and allowed to solidify. It finds use in making pillars, and for making parts of machinery that are not to be subjected to shock. The greater part of it finds use in the manufacture of steel.

**528. How Wrought Iron Is Made.** Since wrought iron contains less carbon than cast iron, it is made by heating cast iron in a reverberatory furnace lined with iron oxide. (See Fig. 301.) The fuel is burned on a fore-hearth, and the hot flames and gases are *reflected* down upon the charge in the furnace. The impurities that were present in the cast iron are gradually oxidized and disappear as gaseous products, or they may combine with the basic material with which the furnace is lined. The carbon in the cast iron unites with the oxygen from the iron oxide and escapes into the air as carbon dioxide or monoxide. As the heating proceeds, the molten mass becomes pasty, because pure iron

has a higher melting point than the cast iron. The process of making wrought iron is known as *puddling*. The pasty mass is worked into large balls called *blooms*. Dripping with slag, they are removed from the furnace and worked under a triphammer or in squeezers to remove the slag and to make the metal somewhat fibrous.

**529. Composition, Properties, and Uses of Wrought Iron.** The purest form of iron on the market is wrought iron. It

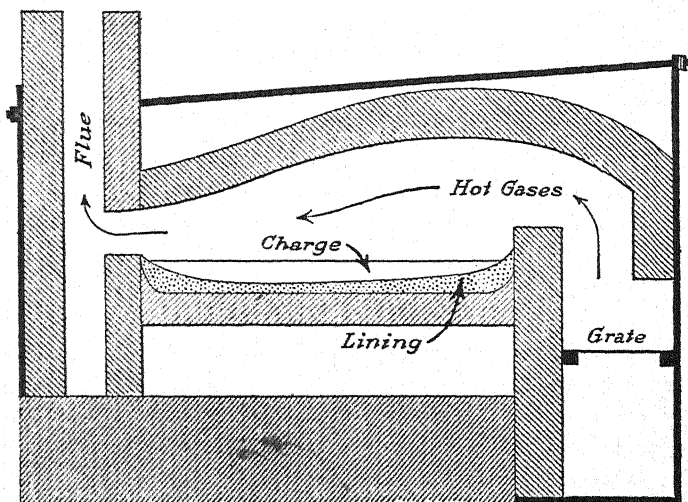


FIG. 301. — Reverberatory furnace. The hot gases are deflected downward upon the charge.

contains less than 0.3% of carbon and small quantities of entrained slag. Wrought iron is soft, fibrous, ductile, and malleable. It softens gradually when it is heated. For that reason two pieces of wrought iron may be heated nearly to the melting point, laid one upon the other, and hammered until they become *welded* into one piece. Wrought iron is very tenacious, but it cannot be tempered. Formerly wrought iron was much used for blacksmith iron, chains,

and wire. Now mild steel is used for such purposes, because it is much cheaper to make steel than to make wrought iron. One of the most extensive uses of wrought iron, however, is in the manufacture of *high-grade steel*. Wrought iron resists corrosion better than either cast iron or steel.

**530. How Steel Differs from Wrought Iron and from Cast Iron.** Steel contains less carbon than cast iron, and more than wrought iron. It varies in composition, containing from 0.2% to 2% of carbon. What is called low-carbon steel usually contains less than 0.8% of carbon; high carbon steel contains from 0.8% to 2% of carbon. The properties of steel vary with the carbon content. The hardness increases as the per cent of carbon increases. Low carbon steel is soft, tenacious, ductile, malleable, and it can be welded easily. High carbon steel is hard and brittle. It may be tempered, but it can be welded only with difficulty. The melting point of steel is lower than that of wrought iron, but higher than that of cast iron. Steel is an alloy that finds use in the manufacture of automobiles, rails, railway carriages, armor plate, guns, projectiles, bridge material, and for other structures.

**531. How Steel Is Made.** Steel has less carbon than cast iron; hence it can be made by burning out the excess carbon of cast iron, or by removing it in some other manner. Steel has more carbon than wrought iron. For that reason steel can be made from wrought iron, if some successful method of adding the required amount of carbon can be found. Both methods of making steel have been used. In the *Bessemer* and *open hearth processes* the manufacturer starts with cast iron direct from the blast furnace. In the old *cementation process* the wrought iron was packed in charcoal and heated. This process is not used in the United States, but it is interesting to compare it with *case-hardening*. (See Section 539.) The *crucible process*, which is practically obsolete in the United States, yields a high grade steel by

heating wrought iron in graphite (carbon) crucibles until a sufficient quantity of carbon is absorbed, from the walls of the crucible and from the carbon mixed with the charge, to give a steel of the desired quality. Either cast iron or wrought iron may be used for making steel in the *electric furnace*.

**532. The Bessemer Process.** Many persons scoffed when the idea of blowing a blast of cold air through molten cast iron was first suggested. But Sir Henry Bessemer, an English inventor, believed that the heat from the chemical action between the oxygen and the carbon and other impurities

in the cast iron would be sufficient to keep the iron from solidifying. When he tried the experiment, he found that the temperature really increases.

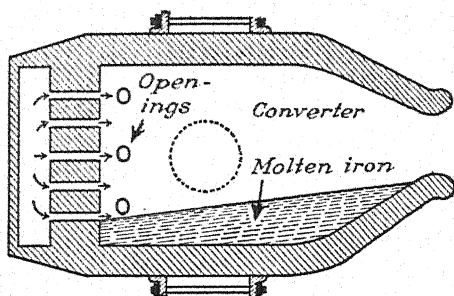


FIG. 303. — Bessemer converter, on its side.

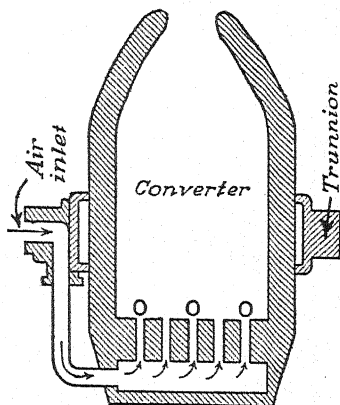


FIG. 302. — Bessemer converter, erect.

In the Bessemer process for making steel the cast iron direct from the blast furnace is poured into a large, egg-shaped converter that holds from fifteen to

twenty tons. The converter is built of wrought-iron plates and lined with fire-brick. It is mounted on trunnions so it may be kept in a vertical position, or turned down upon its

side. (See Figs. 302 and 303.) There are many holes in the bottom of the converter through which air may enter and find its way up through the molten iron in many fine jets. The oxygen unites with the silicon, the carbon, and other impurities present, and the products escape as gases. In from fifteen to twenty minutes, the reaction is complete,

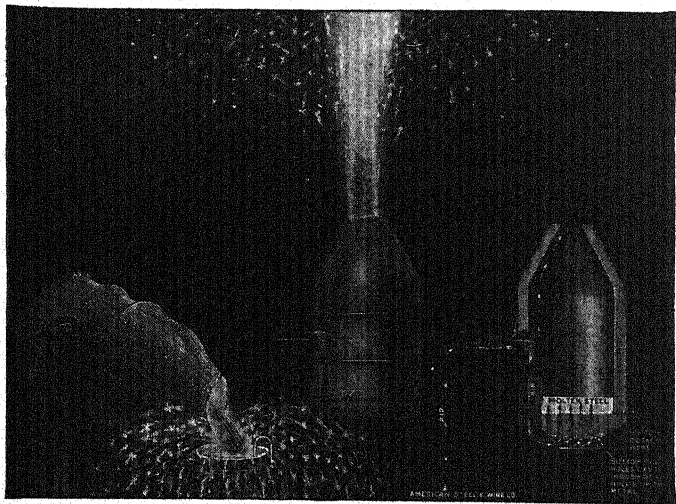


FIG. 304. — Sectional view of the converter at right. During the "blow" shown at center. Converter at left pouring.

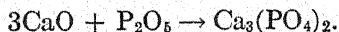
and it must be stopped to prevent oxidation of the iron. The converter is turned down on its side, and *spiegeleisen* or *ferromanganese* is added to the iron in the converter. These alloys are both rich in manganese and carbon, and one of them is added in sufficient quantity to make a steel having the desired per cent of carbon. The manganese unites with any oxygen left in the steel and prevents the formation of "blowholes." Figure 304 shows a Bessemer converter in action; it affords one of the prettiest sights in modern industry as a sheet of flame leaps from the mouth

of the converter and a shower of sparks is sprinkled over a radius of 40 to 50 feet.

**533. Bessemer's Problems.** In working out industrial operations, many problems arise. In making fifteen tons of steel in as many minutes, Bessemer found it quite impossible to tell when to shut off the air blast in order to leave in the steel just the right amount of carbon. His friend, Robert Mushet, suggested that he burn it all out and then add a small quantity of iron that is rich in carbon. When tried, the new plan worked satisfactorily. Hence the addition of *spiegeleisen* or *ferromanganese* in the Bessemer process.

Then, too, the Bessemer process yielded a good steel when Bessemer started with cast iron made from ores that contained only a *small* per cent of phosphorus. *Phosphorus* makes steel brittle when it is cold; it is said to make the steel "cold-short." *Sulfur* present in steel makes the steel "hot-short"; or it makes the steel brittle when it is hot. In the original Bessemer process the converter had been lined with silica,  $\text{SiO}_2$ , which acts as an *acid* anhydride. It will not combine with either the oxide of phosphorus or the oxide of sulfur that is formed when an air blast is forced through cast iron containing phosphorus and sulfur. In other words, the "acid Bessemer process," in which the converter is lined with an acid anhydride, works with iron ores that are nearly phosphorus-free, but it does not give a satisfactory product with ores that contain considerable phosphorus.

To get rid of the phosphorus was a problem for the chemist. It was solved by the English chemists Thomas and Gilchrist. Instead of using silica as a lining for the Bessemer converter, they used dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ). When these carbonates are heated they yield basic oxides,  $\text{CaO}$  and  $\text{MgO}$ . They unite with the phosphorus pentoxide as represented by the following equation:



Of course some magnesium phosphate is also formed. This method of removing phosphorus from the iron used in making steel is known as the Thomas-Gilchrist process. It is also known as the "*basic Bessemer process*." The slag that is formed is rich in phosphorus and it finds use as a fertilizer.

**534. The Open-Hearth Process.** (Siemens-Martin.) In the United States those ores that contain *little* phosphorus find use for making steel by the "*acid Bessemer process*."

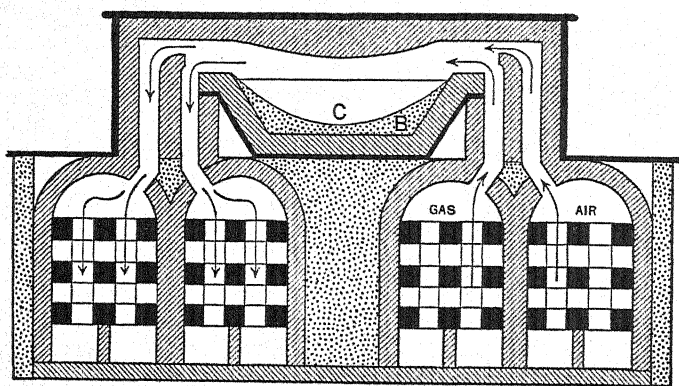


FIG. 305. — Open-hearth process of making steel.

The "*basic Bessemer process*" is little used in the United States. But iron ores that contain considerable phosphorus are made into steel by the use of the "*basic open-hearth process*." A *regenerative* furnace is used.

The *regenerative furnace* was invented by an English metallurgist, Sir William Siemens. Both the air and the gas are pre-heated before the gas is burned. Thus a higher temperature is produced. The gas and air enter the furnace by coming through a checker-work of heated fire-brick. As they burn, the charge on the bed of the furnace is heated by the flames which are reflected down upon the bed of the furnace. (See Figs. 305 and 306.) The *hot waste* products of com-



bustion go out of the furnace through a second checker-work of fire-brick. They heat these brick, just as our chimneys are heated by the hot waste gases that pass up through them. At intervals of about twenty minutes, the direction of the valves is reversed in order to have the incoming gas and air

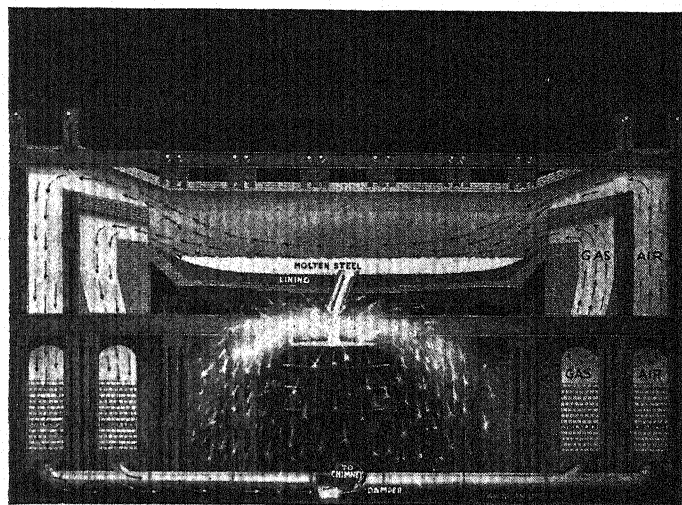


FIG. 306. — Open-hearth steel pouring into ladle.

enter through the checker-work that was just heated. Thus a hot flame is continuously supplied by the union of the pre-heated gas and air. An *open-hearth furnace* is built up of metal plates lined with silica for the acid process, or with basic oxides for the basic process. They are usually from 12 to 15 ft. wide, from 30 to 80 ft. long, and about 2 ft. deep. They are capable of making from 50 to 125 tons of steel at a time.

The *charge* consists of the molten cast iron direct from the blast furnace. It is poured from ladles into the furnace. Then a charging machine picks up a container of *scrap steel*,

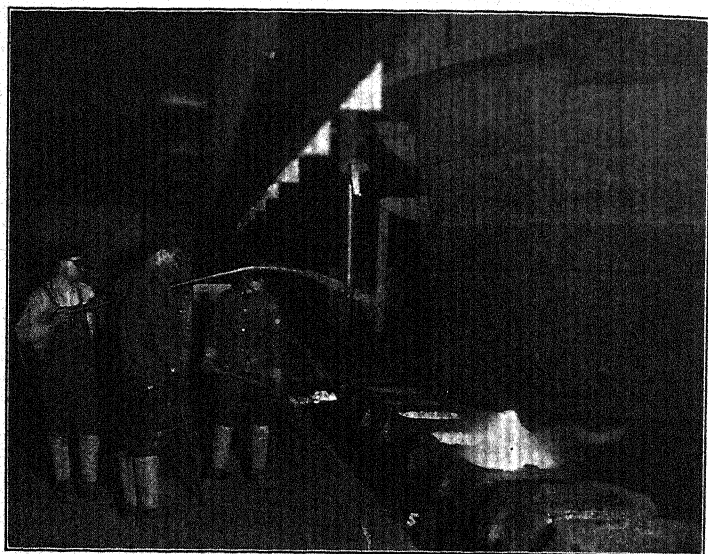


FIG. 307. — Pouring the molten steel into the ingot molds.

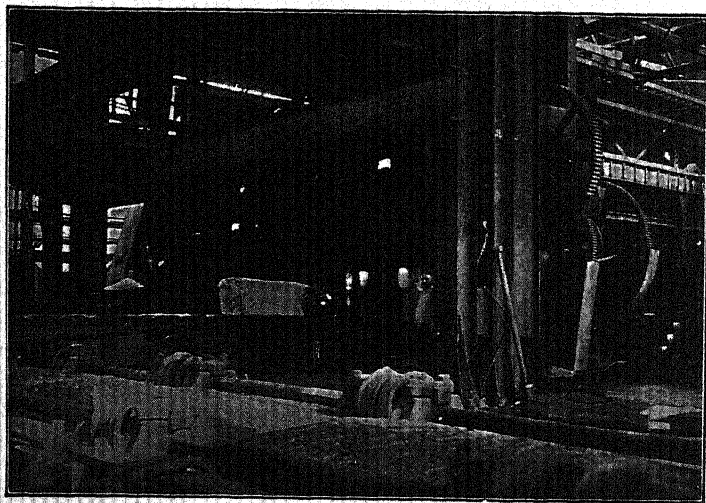
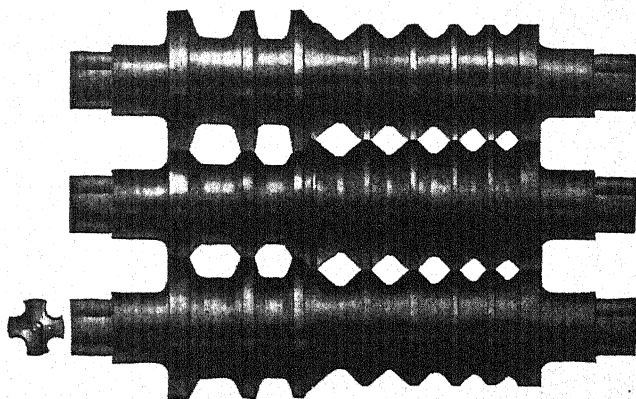


FIG. 308. — Steel ingot about to enter rolls.

## THE ELECTRIC PROCESS OF MAKING STEEL 603

iron ore, and limestone, pushes it into the furnace, and dumps it. The process is economical, since it utilizes the scrap steel, and the oxygen from the iron ore is utilized in the removal of the carbon from the cast iron. The basic material unites with the phosphorus and forms a slag. In some cases, the furnace is tilted forward to pour out the molten steel. Figure 307 shows the pouring of steel into ingot molds. After



*Courtesy of Scientific American*

FIG. 309. — Roughing rolls for making bars for shrapnel.

it solidifies, the ingot is *stripped* and rolled into the desired shape. (See Figs. 308 and 309.)

The furnace for making open-hearth steel was devised by Siemens, but the process was worked out by the Martin brothers of France. It requires from six to twelve hours to make steel by this process. Hence it is possible to take out samples from time to time and send them to the laboratories to be analyzed and tested. The great bulk of the steel made in the United States is made by this process.

**535. The Electric Process of Making Steel.** This process is usually one that deals in refining steel, although steel can be made directly from various materials by means of the

electric furnace. Several types of electric furnaces are in use. In the Heroult furnace (Fig. 310), two carbon electrodes extend through the top of the furnace. The furnace is lined with dolomite. The charge may consist of steel to be refined, or it may consist of scrap steel, cast iron, and iron ore. In fact, such a furnace

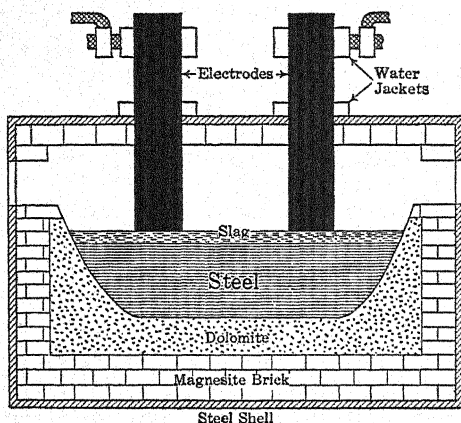


FIG. 310. — Electric furnace.

may be so charged that steel can be made from almost any form of iron or iron ore. When the current is turned on, it arcs across through the slag, flows through the iron and back across the slag again to the other electrode. The current of about 12,000 amperes produces the heat needed to re-

fine the steel. There is no electrolysis. The electric current is used only to supply the heat. The steel that is produced is very high grade, because it is easy to regulate the process and because the process is not carried on in an oxidizing atmosphere. From 5 to 20 tons of steel are made at one time. The operation requires about three or four hours. Figure 311 shows an electric furnace in the act of pouring.

**536. How Two Processes Are Combined.** Two processes are often used in making steel. The Bessemer process is first used because of its speed. Before the reaction is complete, the charge is poured from the converter and transferred either to an open-hearth furnace or to an electric furnace. Then it is finished more slowly. The impurities

are more completely removed and the process is better controlled, because samples can be removed periodically to be sent to the testing laboratories.

**537. How Steel Is Purified.** In making steel there is a tendency near the end of the process toward the formation

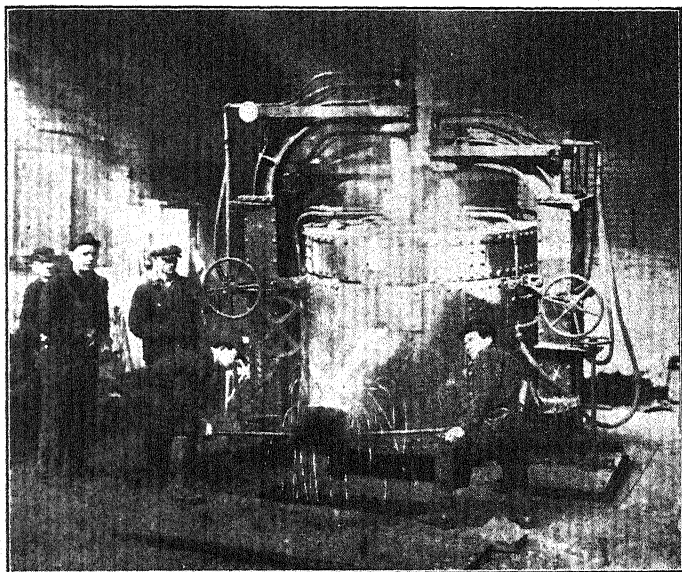


FIG. 311. — Electric furnace (pouring).

of oxides. Gases trapped in the steel tend to form "blow-holes." Even when the steel is rolled, pressed, or hammered, the oxidized surfaces of such "blowholes" will not weld together. To prevent the formation of oxides and to remove gases, some metal that has a greater affinity for oxygen than iron has is added. Such metals are known as purges or *purifiers*. Aluminum, titanium, manganese, and vanadium are used. *Titanium* is especially desirable, because it is one of the few metals that will unite with either the oxygen or

the nitrogen that may be left in the steel. When added to the extent of 10% to 15%, titanium makes the steel homogeneous and increases its wearing qualities 40% or more.

**538. How Steel Is Tempered.** The properties of steel depend not only upon the per cent of carbon it contains, but also upon the manner in which the carbon is held. A *mild steel* having as low as 0.2% carbon resembles wrought iron and it is often substituted for it. Such steel cannot be tempered. *Low-carbon steel* contains from 0.2% to 0.8% of carbon, so small an amount that it cannot be tempered. *High-carbon steel* contains from 0.8% to 2.0% of carbon. Such a steel can be tempered, but it is difficult to weld.

If a high-carbon steel is heated above 670° C., or to a bright cherry heat, a carbide of iron is formed. It dissolves in the iron that is present. If such a solution is cooled *quickly* by plunging it into water or some other cooling medium, the carbide does not separate. A very hard steel results, but it is decidedly brittle. If the solution of iron carbide in iron is cooled *slowly*, some of the iron carbide decomposes and a mixture of *iron carbide*, *iron*, and *graphite* results. Such a mixture is soft and tough. All grades of hardness between these extremes may be obtained by *reheating* a hardened steel to a *definite* temperature, and then cooling it quickly. For example, a piece of steel is heated to a bright red heat, and then cooled by plunging it into cold water. It will be hard, but very brittle. If it is reheated to about 220° C., and then cooled quickly, it will not be quite so brittle. Such a process is known as *tempering*. It will be hard enough for use in making razor blades. If reheated to about 280° C. and then cooled quickly, it becomes much more flexible. Such a steel is suitable for watch springs or sword blades. If we reheat the steel to from 300° to 350° C., more of the iron carbide decomposes, and the tempered steel, formed by quickly cooling the product, is suitable for making hand saws and other wood-working tools. Sometimes in



making edged tools, such as chisels, only the tip is cooled at first. Then heat flows slowly into the tip from the uncooled portion until it has the proper temperature. At that instant the whole piece of steel is cooled quickly. The workman sometimes determines the correct temperature from the color of the oxide that is formed when the steel is reheated. Delicate pyrometers are used in large plants to measure the exact temperature. The quality of the steel varies with the medium used for cooling. Steels are quenched, for example, in cold water, hot water, oil, and certain melted salts.

**539. How a Soft Steel Is Case Hardened.** Sometimes a tough steel must have a hard surface. It is possible to start with a soft, low-carbon steel and to harden its surface by packing it in charcoal, sodium cyanide, or scrap carbonaceous material, and heating it until sufficient carbon is absorbed at the surface to give it the desired surface hardness. This method of forming a hard surface skin or layer of high-carbon steel on a soft, tough core is known as *case hardening*. The surface of a case hardened steel resists wear, and the tough core makes the steel less likely to break under strain.

**540. How Steels Are Tested.** In the slower processes of making steel, samples of the product are taken from the furnace from time to time and sent to the chemist for analysis. He may determine the per cent of phosphorus, the per cent of carbon, the per cent of manganese, and the per cent of sulfur. Other samples may go to the physical laboratory where they are tested for hardness, tensile strength, crushing strength, and elasticity. Special tests are made when the steel is to be used for special purposes. For example, in testing freight car axles, the axle is laid upon two supports placed about two feet apart, and a weight of 2600 lb. is dropped upon the axle from a height of more than 40 ft. The axle is not supposed to crack when subjected to such blows three times in succession. But neither the physical test nor the chemical tests will show the presence of blowholes.



The microscope is now much used to tell what properties a sample of steel will have. A sample is ground to give a flat surface, etched with an acid, and then photographed when highly magnified. An expert in photomicrography can tell a great deal about the properties of steel and other metals from photomicrographs. (See Figs. 312 to 317, inclusive.)

**541. Special Steels.** Certain metals added to steel form alloys that have special properties which fit them for particular purposes. Ordinary carbon steel is an alloy, but the name *alloy steel* is given to these special alloys. The metals are usually added to the steel just before it is drawn from

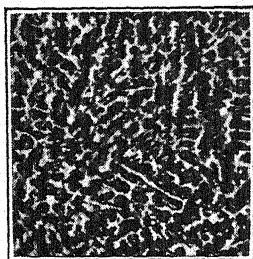


FIG. 312. — Cast iron  
(100 diam.).

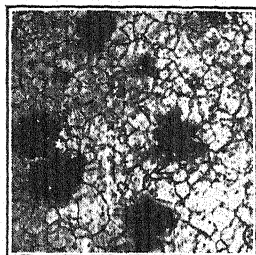


FIG. 313. — Cast iron  
(annealed).

the furnace. For special uses in the automobile and airplane industries new alloys are always in demand.

*Nickel steel* made its appearance shortly after the battle of the *Monitor* and the *Merrimac*. It may contain 4% or more of nickel. Such an alloy steel is not easily corroded, and it combines toughness with hardness. It is strong and elastic. It finds use in making armor plate, automobile parts, and bridge materials. *Invar* is a nickel steel alloy that contains about 36% of nickel. It is little affected by changes in temperature; hence it finds use in making measuring tapes, pendulums for clocks, and automobile parts. *Permalloy* contains about 80% of nickel. It is so easily magnetized that a bar of it becomes a magnet when it is held

in a North and South direction and iron filings will cling to it. When it is turned to an East and West direction the bar loses its magnetism, and the filings fall off.



FIG. 314. — Wrought iron showing slag (100 diam.).



FIG. 315. — Wrought iron (reheated).

*Chrome steel* is exceedingly hard and tough. It finds use in making ball and roller bearings, and for the jaws of crushing machinery. When the amount of chromium used reaches from 6% to 14%, the alloy is known as "stainless steel."

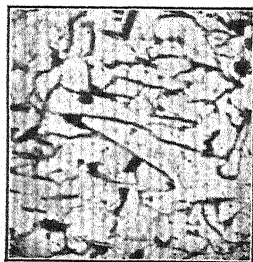


FIG. 316. — Steel magnified (100 diam.).

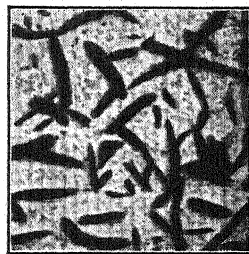


FIG. 317. — Steel after reheating.

It resists corrosion remarkably well. Hence it finds use in making knives, cooking utensils, surgical instruments, golf clubs, and various metal fittings.

*Nickel-chromium steel* contains both nickel and chromium, usually about 4% of each one. It is hard and tough, suitable for making plowshares, armor plate, crankshafts, files, and

gear teeth. *Staybright steel* contains 18% of chromium and 8% of nickel. It does not tarnish. It is sold under the trade name of *Allegheny metal*.

*Chromium-vanadium steel* has a very high tensile strength. It is used in making automobile parts that must be subjected to severe strains and shocks. A thin strip of good vanadium steel may be bent nearly double without breaking.

*Manganese steel* is exceedingly hard, even when it is cooled slowly. The first specimens were so hard that no tool would cut them and they were as brittle as glass. Such steels are now made that are still extremely hard, but not so brittle. They find use in making burglar-proof safes, jaws for stone crushers, and teeth for steam shovels. During the World War, manganese steel was used for making helmets.

*Silicon steel* is very flexible. It finds use in making automobile springs. It is also used for making the cores of transformers and electromagnets, because it is easily magnetized, and it loses its magnetism easily. Cast iron that contains considerable quantities of silicon is very resistant to corrosion and to the action of acids. *Duriron* is an alloy that contains from 12% to 15% of silicon. It finds use for making pipes and liquid containers that resist the action of moist air or dilute acids.

*Tungsten steel* contains rather a high percentage of tungsten and sometimes chromium. It may be heated to a red heat and cooled in the air without losing its temper. Hence it is known as *air-cooled*, or *self-tempering* steel. When used as a lathe tool, for cutting other metals, this steel will retain its hardness even when it is heated red hot by friction. It is often called "high-speed" steel, since tools made of it can cut about ten times as fast as the old lathe tools. *Molybdenum* is often used instead of tungsten for making "high-speed" steels. High-speed steels sometimes contain cobalt. They are called "super-high speed" steels. Cobalt alloy steels are now used in making permanent magnets. They

retain their magnetism, and they are more powerful than magnets made of other substances.

*Nitralloy steels* are made by treating a special steel, which contains a little aluminum, with ammonia gas at a temperature of about  $500^{\circ}\text{C}$ . for a certain length of time. It is extremely hard and it is not corroded by either fresh or salt water. When used in motors, it reduces wear and cuts down oil consumption, because its surface is so smooth and hard. The reduction in friction permits motors to be run at a greater speed if this steel is used.

**542. Properties of Iron.** Pure iron is so rare that its properties have little interest for us. It is a silver-white metal, soft, tough, and ductile. It does not tarnish readily. Iron that is used commercially varies in its properties, because it contains carbon and other impurities in varying amounts. All forms, however, *corrode* or *rust* in moist air.

The corrosion of iron is a complex process. It is probable that a basic carbonate is first formed, and that it decomposes and forms a *hydrated oxide*, which is the final product in the corrosion of iron. Iron rust is brittle, and it scales off, exposing the metal underneath to the agents of corrosion. Therefore iron is *not a self-protective* metal. In fact, the rust seems to act as a catalyst to form more rust, until the entire piece is finally converted into iron oxide. Acids accelerate corrosion, but alkalis retard it.

In some cases the corrosion of iron seems to be an electrical process. A carbon particle in contact with a piece of iron will cause the iron to rust rapidly. The carbon acts like the positive plate of a miniature voltaic cell, and the iron becomes the negative plate. Moisture dissolves carbon dioxide from the air and serves as the electrolyte. The iron, which really becomes the negative plate, goes into solution rapidly. Cinder concrete is responsible for the rapid rusting of the pipes in many bath rooms. Cement mortar placed next to the pipes will protect them.

Dilute acids act readily upon iron, but alkalis have no effect upon it. Concentrated nitric and sulfuric acids do not attack iron. In fact, dipping iron into concentrated nitric acid renders the iron *passive*, or *inactive*, with respect to its behavior toward other chemicals.

**543. How Can Iron Be Protected?** It is unfortunate that our most useful metal rusts so rapidly that methods of protecting it must be used. A few of the common methods are discussed here:

1. *Coating it with other metals.* We have already learned that iron is pickled in acids to remove any coating of oxide, and then coated with certain metals, either by the dipping process or by plating. *Zinc* is the metal used for galvanizing. In making tinware, sheet iron is covered with a thin layer of *tin*. Finely powdered *aluminum* is used for silvering radiators. Iron is plated with *nickel* or with *chromium*.

2. *Coating it with non-metals, or metallic compounds.* Iron that is kept well-painted does not rust, but certain kinds of paint accelerate corrosion. In making *enamel-ware* a special mixture of borates and silicates is fused, granulated in cold water, and then finely powdered. The iron is thoroughly cleaned and then dipped into a suspension of this powder in water. It is then heated in a furnace until the powder melts and forms a glaze on the surface of the iron. *Lacquers* and *varnishes* are also used to prevent the rusting of iron.

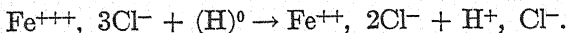
3. *Alloying the iron with other metals.* *Silicon alloys* have been mentioned. There are several types of *stainless steel* on the market. They contain from 6% to 14% of chromium. *Allegheny metal* does not tarnish. It contains 18% of chromium, and 8% of nickel.

4. *Using chemicals to form a surface coating.* When a blacksmith heats a piece of iron, a black scale of ferrous-ferri oxide,  $\text{Fe}_3\text{O}_4$ , is formed at the surface. It is adherent and non-porous. By treating red-hot iron with steam, a thin coating of this oxide is formed. Under the name of

*Russia iron* it is produced artificially on locomotives, stoves, stovepipes, etc., to prevent corrosion. It scales off, if the iron is pounded. Iron is *Parkerized* by dipping it into a hot alkaline solution of sodium phosphate. This covers the iron with a protective coat of what is believed to be basic phosphate of iron. The coat is so thin that the size is practically unchanged.

**544. The Oxides of Iron.** Of the three oxides of iron, *ferrous oxide*,  $\text{FeO}$ , is of little importance, since it changes rapidly when exposed to the air, and forms *ferric oxide*,  $\text{Fe}_2\text{O}_3$ . This oxide is not only the most important ore of iron, but it finds use as a cheap red paint sold under the name of *red ocher*, *Venetian red*, or *Indian red*. *Rouge* is a form of iron oxide that is used as a pigment and for polishing. *Limonite* is a natural *hydrated ferric oxide* that is pulverized and used as a pigment under the name *yellow ocher*. When heated or roasted it forms the *siennas* and *umbers*. *Prince's mineral*, which forms an excellent paint for metal roofs, is made by calcining a hydrated oxide or carbonate of iron that contains some earthy material. *Ferroso-ferric oxide*,  $\text{Fe}_3\text{O}_4$ , was discussed in the preceding section.

**545. Oxidation and Reduction Are Related to Valence Changes.** Two chlorides of iron are known. In *ferrous chloride*,  $\text{FeCl}_2$ , the valence of the iron is 2; in *ferric chloride*,  $\text{FeCl}_3$ , the valence of the iron is 3. If we treat a solution of ferric chloride with nascent hydrogen, the ferric chloride is *reduced* to ferrous chloride, and the valence of the iron is *lowered* from 3 to 2. The equation follows:



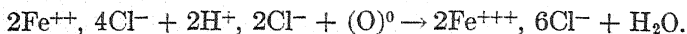
This is an example of reduction in which no oxygen is abstracted from the compound at all. The valence of the iron is lowered. *We may define reduction as a chemical reaction that involves a lowering of the valence of the positive element.* From the standpoint of the ionic theory, *reduction*

is accomplished when a positive ion gains a negative charge. For example,

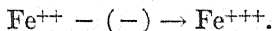


In terms of the *electron* theory of valence, a *positive element* is *reduced* when it gains one or more electrons.

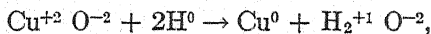
Conversely, we can oxidize ferrous chloride to ferric chloride by heating it with an oxidizing agent in the presence of hydrochloric acid:



In this case the valence of the iron is increased from 2 to 3. *Oxidation* may be defined as a chemical reaction that involves an increase in the valence of the positive element. In terms of the ionic theory, an ion is oxidized when it loses a negative charge.



Based upon the electron theory of valence, an element is oxidized if it loses one or more electrons, and reduced if it gains one or more electrons. In the simple equation,



we see that the copper, in being *reduced*, has its valence lowered from + 2 to zero. The hydrogen, in being *oxidized*, has its valence raised from zero to + 1.

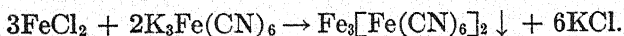
**546. Will "ous" or "ic" Compound Be Formed?** If we treat iron with dilute hydrochloric acid, ferrous chloride will be produced. Hydrogen, which is a reducing agent, is liberated during the reaction, and it keeps the iron reduced to the "ous" condition. For the same reason, ferrous sulfate is formed by the interaction of dilute sulfuric acid on iron. Ferric salts are formed when oxidizing agents are present. Hydrogen peroxide added to a solution of ferrous sulfate will oxidize it to ferric sulfate.



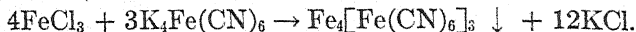
★ 547. **Other Compounds of Iron.** *Ferrous sulfate*,  $\text{FeSO}_4$ , is obtained as a by-product by concentrating the solutions used for cleaning iron or steel that is to be dipped or plated. It forms light green crystals known as *copperas*, or *green vitriol*. It finds use as a mordant, for making black inks, and as a spray for destroying weeds. *Ferric chloride*,  $\text{FeCl}_3$ , is used in medicine. Absorbent cotton, dipped into a solution of ferric chloride, forms *styptic cotton*. When put on a wound it stanches the flow of blood and it also serves as an antiseptic.

★ 548. **Inks.** If we add to a freshly prepared solution of ferrous sulfate a solution of tannic acid, the nearly colorless compound, *ferrous tannate*, is formed. It slowly oxidizes to form the black compound, *ferric tannate*. Iron inks contain ferrous tannate, dextrin, some poisonous compound to prevent the growth of mold, and usually a little dye to give the ink a temporary color until the ferrous tannate is oxidized to ferric tannate to produce a permanent color. Many of the inks now used are solutions of aniline dyes. A third class of inks, of which printer's ink is a common example, is made from lampblack and some material to serve as a binder. Iron inks are easily removed by the use of a reducing agent, but the other types cannot be removed by this method. Sodium hypochlorite is used extensively for removing ink stains. *It must never be used on colored fabrics or on silk.* Skimmed milk applied at once to fresh ink stains and then followed by cold water will usually remove nearly all the stain.

549. **Tests for Iron.** If we add to a solution of a *ferrous* salt a few drops of a solution of *potassium ferricyanide*,  $\text{K}_3\text{Fe}(\text{CN})_6$ , commonly called *red prussiate of potash*, a dark blue precipitate is formed. This blue substance is known as ferrous ferricyanide; it is used as a pigment under the name of *Turnbull's blue*. Since the reaction occurs only when ferrous ions are present, it serves as a test for *ferrous* iron.



A dark blue precipitate is also obtained by mixing solutions of a *ferric salt* and *potassium ferrocyanide*,  $K_4Fe(CN)_6$ , or the *yellow prussiate of potash*.



This reaction takes place when ferric ions are present, and it serves as a *test for ferric iron*. The precipitate, known as *Prussian blue*, is used as a pigment. It is sometimes used as laundry blue. If the clothes have not been rinsed free from alkaline soaps, their alkalis will decompose this blue compound, precipitating *ferric hydroxide* on the fibers and forming iron rust spots.

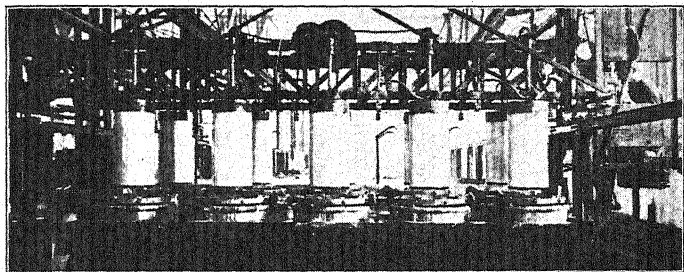
★ 550. **Blueprints.** Solutions of ferric salts form only a brown solution when mixed with potassium ferricyanide. Blueprints are made by coating in the dark a well-sized paper with a mixture of the solutions of *ferric ammonium citrate* and *potassium ferricyanide*. After the paper is dry it is then placed under the negative and exposed to the light. Wherever the light strikes the paper, reduction occurs and a ferrous salt is produced. The reduction proceeds more rapidly where the light is strongest. The print is developed by dipping it into water; then any *ferrous salt* formed by reduction reacts with the *ferricyanide* to form Turnbull's blue. Where no light strikes the print, no reduction occurs and the water washes away the unchanged mixture, thus fixing the print. The exposed portions will be blue in color and the unexposed parts will be white.

## B. NICKEL AND ITS COMPOUNDS

551. **Nickel.** Some nickel is found in the United States, but Ontario, Canada, produces nearly all our supply. Nickel is a hard silver-white metal, capable of receiving a high polish. It does not tarnish easily. In its chemical properties nickel resembles iron, although it is not nearly so active.

**552. Uses of Nickel.** Considerable nickel is used as a coating to prevent the rusting of iron. Some nickel is used in hydrogenating oils, and we know that large quantities find use in making nickel steels. (See Fig. 318).

The *nickel coins* are alloys containing about 20% nickel, the remaining constituents being mainly copper. *Monel metal* is made directly from a complex ore of nickel. It consists of about 67% nickel, 28% copper, and small quantities of iron and manganese. This alloy is strong and tough, and



Courtesy Edison Storage Battery Co.

FIG. 318. — To make nickel flake, the revolving cylinders are plated with alternate layers of nickel and copper. Then the copper is dissolved in acid and the thin nickel sheets are shredded.

it resists the action of the air and of acids. It finds use in making valves for steam engines, and in making screens for filtering chemicals. It makes almost ideal fly screens for doors and windows. *Nichrome* is a valuable alloy of nickel, chromium, iron, and manganese. This alloy melts only at a very high temperature and it has a very high resistance to the passage of an electric current. Hence nichrome is used for making electric flatirons, toasters, and heaters. It forms excellent boxes for use in case-hardening steels.

★ **553. Nickel Compounds.** This metal forms *nickelous* and *nickelic* salts in which the valence of nickel is 2 and 3 respectively. Nickelous salts are more common; they usually crystallize as beautiful green crystals. Nickel flake and

nickelous oxide are used for making the positive plate in the Edison storage battery. In charging such a battery the nickelous oxide is oxidized to the nickelic. *Nickelous ammonium sulfate* is used as the electrolyte in nickel plating.

### C. COBALT AND ITS COMPOUNDS

**554. Cobalt.** This metal so closely resembles nickel that they are often called the twin metals. It has been used in some cases to plate iron, but it is quite expensive. One of the alloys of cobalt is *stellite*, which consists mainly of *cobalt* and *chromium*. This alloy finds use in making "stainless" cutlery, since it is very resistant to acids. It is a competitor of tungsten steel for use in lathes for cutting metals at high speed.

*Carboloy* is made by combining cobalt with a carbide of tungsten. It is the hardest material manufactured for use in making cutting tools. Carboloy is hard enough to cut threads on glass and to bore holes through glass or porcelain. As a lathe tool for cutting metals, it may be used for high-speed work, since it is not a steel, and it has no "temper." It is a tough alloy, and not easily broken.

★ **555. Cobalt Compounds.** Like nickel and iron, cobalt has a valence of 2 or 3. The cobaltous compounds, which exist as red crystals that form pink or red solutions, are the more common. Since cobalt compounds are red when hydrated and blue when anhydrous, *cobalt chloride*,  $\text{CoCl}_2$ , is used as a rather crude method of determining the amount of moisture the air contains. Substances coated with its solution change color as the moisture in the air varies. When the relative humidity is high they are pink in color; as the air grows less moist they change to a lavender or blue color. As the blue color is far more intense than the red, cobalt salts form the basis of the so-called *sympathetic* or *invisible inks*. The writing which is done with a dilute solu-

tion is almost colorless until heat is applied; then the more intense blue color shows clearly. *Cobalt nitrate*,  $\text{Co}(\text{NO}_3)_2$ , finds some use in analytical work. Cobalt compounds impart to glass a beautiful blue color. A mixture of the oxides of cobalt, copper, manganese, and silver was used in gas masks during the war under the name of *hopcalite*.

Carbon monoxide is not appreciably adsorbed by activated charcoal in gas masks, but by the action of *hopcalite* it may be oxidized to form the harmless carbon dioxide.

### SUMMARY

The *iron family* includes *iron*, *nickel*, and *cobalt*. The oxides of iron are the chief ores. Minnesota, Michigan, and several other states are large producers of iron ore.

In Minnesota the earth is stripped off, and the loose ore is mined with steam shovels. Shaft mining is used in Michigan.

*Steel* can be made by starting with wrought iron and adding to it the desired amount of carbon. It is usually made by starting with cast iron and removing some of the carbon.

In the Bessemer process the excess carbon is all burned out by means of a blast of air, and *spiegeleisen* or *ferromanganese* is then added to introduce the right amount of manganese and carbon. (See Fig. 319.)

In the *open-hearth process*, cast iron is heated with iron ore until a steel of the desired carbon content is obtained. The process is slow enough so the product may be tested from time to time. Steel is also made in the electric furnace.

When steel is heated, and then cooled quickly, it is very hard and quite brittle. If cooled slowly it becomes soft and tenacious. When hard steel is heated a second time to a certain temperature and then cooled properly, a process known as tempering, steel of any desired degree of hardness between these extremes is produced.

Ordinary iron rusts in moist air, forming a *hydrated oxide*. Iron may be protected by covering it with zinc, tin, or nickel. Aluminum is used as a protective paint. Other methods of protecting iron include the use of lead paints, lacquers, and enamels. A thin

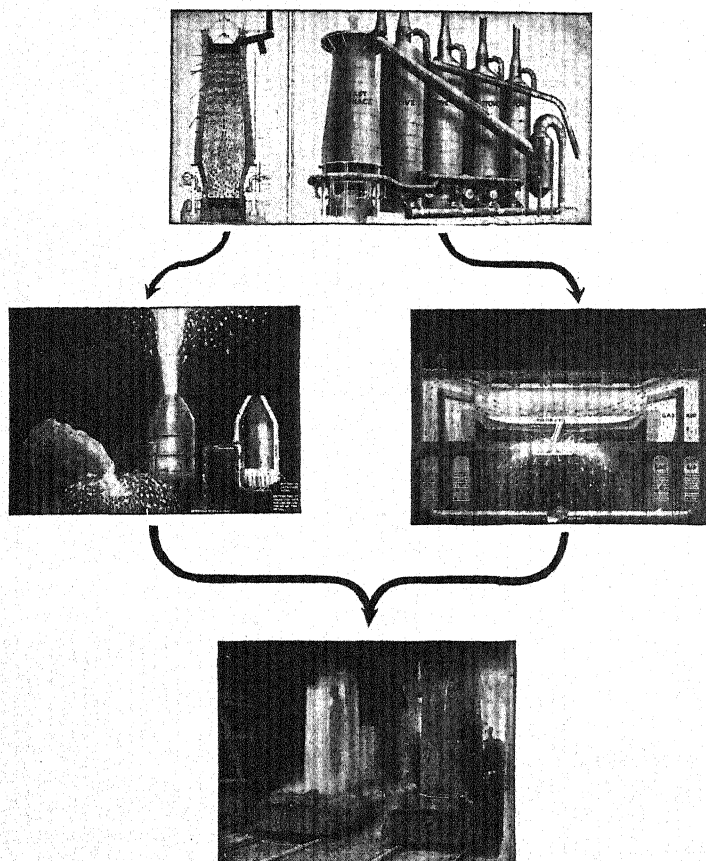


FIG. 319. — From iron ore to the steel ingot. Bessemer steel (left); open-hearth steel (right).

adherent film of magnetic oxide of iron forms when iron is treated with superheated steam. Iron covered with such a protective coat is known as Russia iron. Iron or steel may be Parkerized.

Any chemical change that involves a decrease in the valence of the positive element of a compound is *reduction*. *Oxidation* causes the valence of the positive element to be increased.

*Ferrous sulfate* is used as a mordant, as a spray for weeds, and in the manufacture of ink.

A *ferrous* salt gives a blue color with a *ferricyanide*; a *ferric* salt gives a blue color with a *ferrocyanide*.

## PROPERTIES OF IRON AND STEEL

	Carbon content, per cent	Structure	Hardness	Properties
Cast iron.....	2-5	Crystalline	Very hard	Cannot be welded or tempered
Wrought iron..	0.05-0.3	Fibrous	Soft	Can be welded, but not tempered
Steel (low-carbon)	0.2-0.8	Granular	Moderate	Can be welded, but not tempered
Steel (high-carbon)	0.8-2	Granular	Hard	Can be welded and tempered

## QUESTIONS

## GROUP A

1. Why cannot wrought iron be tempered? Why cannot cast iron be welded? Why is it more difficult to weld a high-carbon steel than it is to weld a low-carbon steel?

2. Compare cast iron, wrought iron, and steel as to composition, properties, and uses.

3. What is the function of a "purifier" in steels?

4. Why would you not expect to find iron occurring free in nature?

5. How would you convert ferric chloride into ferrous chloride?

6. What would happen if you added some hydrogen peroxide to a solution of ferrous sulfate?

7. Which class of iron compounds is more stable when exposed to air? Which would be more stable, the *dry* salts or their *water solutions*?



8. If you were given an iron solution how would you tell whether it contains ferrous or ferric iron?
9. Given a solution of an iron salt. How could you tell whether it is a chloride, a nitrate, or a sulfate?
10. Name three important alloy steels, giving their uses.
11. Name as many ways as you can of protecting iron from corrosion.
12. What kind of iron ore is made into steel by the *acid* Bessemer process?
13. Give two definitions of oxidation. Two of reduction.
14. Why should a black paint not be applied as a protective coating for iron?
15. What is "cinder concrete"? Why should it never come into contact with iron pipes in a plumbing system?
16. Why did the use of alloy steels and case hardening follow rather closely the first battle of iron-clad ships?

## GROUP B

17. What is meant by case-hardening? What is the purpose?
18. Freshly prepared ferric hydroxide is an antidote for arsenic poisoning. How would you prepare this compound? Write the equation for the reaction.
19. Oxalic acid is a reducing agent. What kind of ink stains can be removed by the use of oxalic acid?
20. How would you remove a stain made with an iron ink? Would the same method be useful for removing rust stains made in the laundry from Prussian blue?
21. How are sympathetic inks used?
22. Why have the processes for making steel out of cast iron gradually superseded those of making steel out of wrought iron?
23. What is meant by a regenerative furnace? What are its advantages?
24. Why does not the molten iron in a Bessemer converter solidify when a blast of cold air is blown into the converter?
25. What do you think would be the probable outcome of a war between two nations of equal resources if one of them held the secret of making "high speed" steel? Explain.

## PROBLEMS

## GROUP A

1. How many pounds of iron can be obtained from one ton of ore that is 95% hematite,  $\text{Fe}_2\text{O}_3$ ?
2. How many pounds of iron chloride can be made by dissolving 500 lb. of iron in hydrochloric acid?
3. How many pounds of iron nitrate can be made by dissolving 500 lb. of iron in dilute nitric acid?

## GROUP B

4. A lump of iron weighing 112 gm. is dissolved in hydrochloric acid. How many grams of ferrous chloride will be formed? How many liters of hydrogen will be set free?
5. To 100 gm. of ferric chloride, 40 gm. of sodium hydroxide are added. How many grams of ferric hydroxide are precipitated?
6. How many grams of oxygen will be needed to oxidize 200 gm. of ferrous sulfate to ferric sulfate in an acid solution?

## SUPPLEMENTARY PROJECTS

Prepare a report on one of the following topics:

1. Taylor and White's exhibit of "high speed" steel at the Paris exposition.

Reference: STOUGHTON, BRADLEY, *Metallurgy of Iron and Steel*. McGraw-Hill.

2. Kelly's claims to priority in making steel by use of an air blast.

Reference: *New International Encyclopedia*.

## CHAPTER 37

### COPPER — SILVER — GOLD

#### Vocabulary

**Argentiferous.** Silver-bearing.

**Cupel.** A small, shallow, porous cup or crucible.

**Sized.** Coated with some glutinous material to fill the pores.

**Alluvial.** Alluding to the deposits made by streams or rivers.

**Sluice.** An artificial passage for water.

**Riffles.** Bars or poles laid across the bottom of sluices to intercept the gold.

**Matte.** Crude impure metal, or a mixture of metals, smelted from sulfide ores.

**556. Introductory.** Three metals, *copper*, *silver*, and *gold*, are included in the copper family. All of these metals are found free in nature to some extent. All of them were known to the ancients. They are all soft, dense metals, both malleable and ductile. Silver is the best conductor of heat and electricity known. Copper is second, and gold third. If we refer to the activity series of metals, we find these metals near the bottom of the list. From the periodic table, we observe that the group valence is 1. Copper, however, is more often 2; and gold is usually 3.

#### A. COPPER

**557. Where and How Copper Is Found.** About 60% of the world's output of copper is produced in the United States. Montana produces a little more than one-third, and Arizona and Michigan each about one-third. In northern Michigan native copper is found, sometimes in large masses six feet thick. The Calumet and Hecla mine is world famous. Its

shaft is 8500 ft. long, more than one mile in vertical depth. Usually the copper ore in Michigan is mixed with quartzite rock. (See Fig. 320.) The ore in Montana consists of copper sulfides. *Chalcocite*,  $\text{Cu}_2\text{S}$ , is known as "copper glance." It is very rich in copper. Two double sulfides of copper, *chalcocopyrite* and *bornite*, are important ores. In Arizona, copper occurs in the form of two beautiful minerals, *malachite* and *azurite*. Both are basic carbonates of copper. One is green and the other is azure blue. They are hard and take a high polish. Hence fine specimens are sometimes used for table tops and for ornamental purposes. Gold and silver, together with arsenic and antimony, are usually found associated with copper ores.

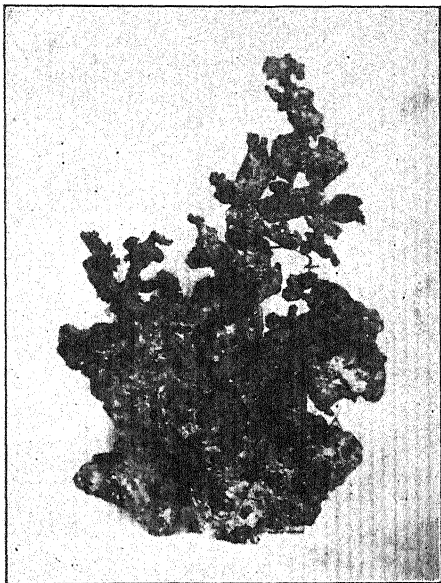


FIG. 320. — Mass of native copper.

★ 558. **Extraction of Copper.** Both the sulfide and the carbonate ores are first roasted to form the oxide of copper, which is then reduced with carbon. When copper is to be extracted from complex iron and copper ores, some method must be used to separate the iron from the copper. Since iron is more active than copper, it will combine with silica to form an iron silicate, or slag. Hence some *roasted ore*, some *unroasted ore*, and *coke* are heated in a blast furnace similar to that used for extracting iron. The bulk of the iron unites with the silica

used to line the furnace. A *matte* consisting largely of cuprous sulfide, with traces of gold, silver, arsenic, and antimony, is formed in the furnace. Both the slag and the matte are then drawn off into a forehearth. The lighter slag floats, and it is removed from the top of the hearth; the matte is

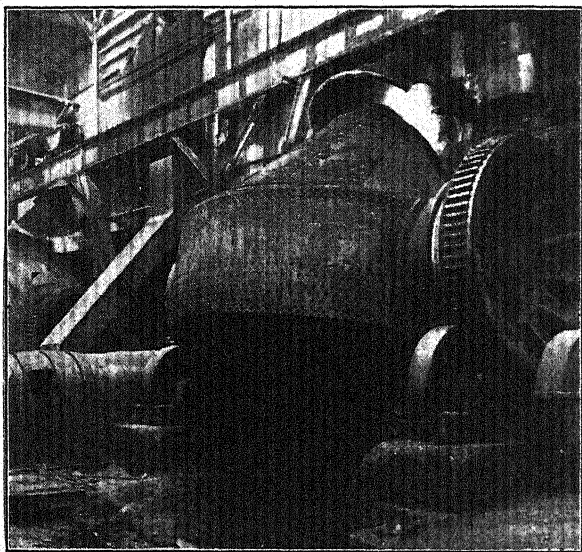


FIG. 321. — Converter used for making blister copper.

drawn off at the bottom. In this manner nearly all the iron is separated from the copper.

★ 559. **How Blister Copper Is Made.** The next step is the making of *blister* copper. The matte is poured into a converter not unlike that used in the Bessemer process. Here the sulfur, arsenic, and antimony are oxidized and volatilized by the air-blast. (See Fig. 321.) Any iron that remains combines with the silica used to line the converter and forms a slag. After the copper is poured from the converter, it is permitted to cool and solidify. As it cools it expels some sulfur

dioxide that had been absorbed. The product is full of bubbles and it is known as blister copper. The silver and gold are still retained by the copper.

★ 560. **The Poling of Copper.** Blister copper contains traces of copper oxide. To remove the oxygen, the molten blister copper is stirred in a reverberatory furnace with long green (freshly cut, or unseasoned) poles. The carbon and the hy-

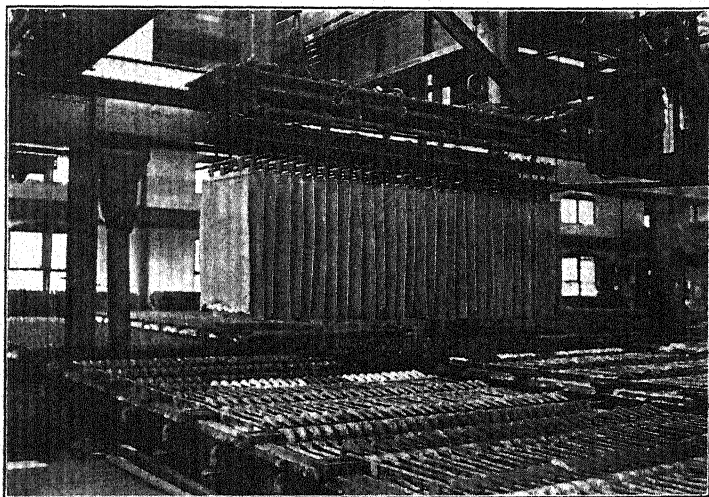


Fig. 322. — Refining copper by electrolysis. A set of electrodes lifted from the electrolytic tank is shown at center.

drocarbons from the freshly cut poles reduce the copper oxide to metallic copper. The *poled* copper is then cast into anode plates to be *refined* by electrolysis.

561. **Refining of Copper.** For two reasons copper is refined before it is put on the market. (1) Appreciable amounts of gold and silver are left in the poled copper. Sometimes the amount of these metals recovered more than pays for the cost of refining. (2) Copper is largely used for making electrical conductors, and small amounts of impurities in-

crease its resistance. Traces of arsenic in copper lower its conductivity decidedly. As low a percentage of iron as 0.4 of 1% decreases the conductivity of copper 64%.

In refining copper, sheets of pure copper form the cathodes and large plates of impure copper the anodes. The electrolyte is a solution of copper sulfate in sulfuric acid. Copper goes into solution at the anode and *pure* copper is deposited at the cathode. (See Fig. 322.) The impurities fall to the

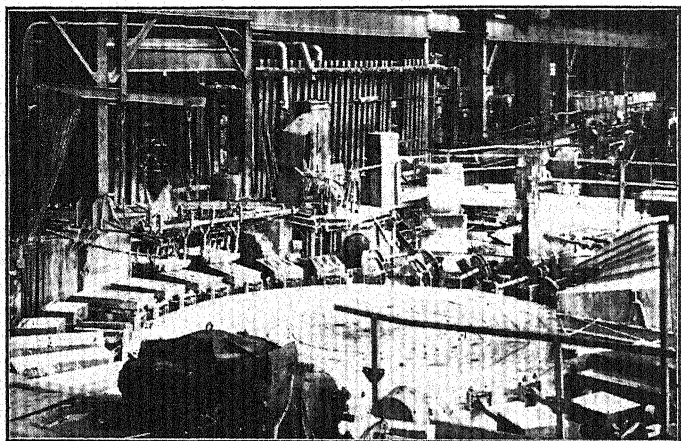


FIG. 323. — Molds in which copper ingots are cast.

bottom of the tank as a mud or slime. The gold and silver are recovered from this slime. Figure 323 shows the rotating table upon which copper ingots are cast in molds.

**562. Properties of Copper.** Copper is a soft, red metal. It is ductile, malleable, and very tenacious. Its specific weight is 8.9. As a conductor of heat and electricity, copper stands next to silver.

Heated in the air, copper forms black *cupric oxide*,  $\text{CuO}$ . The vapor of copper burns with a *green* flame. Copper compounds also burn with a green flame, and their solutions are colored a deep blue by ammonia. Exposed to the action



of sulfur fumes, copper soon becomes covered with a blue-black coating of *copper sulfide*,  $\text{CuS}$ . In moist air copper tarnishes and forms a green basic carbonate. The metal is self-protective, since the tarnish is adherent. Hydrochloric acid does not affect copper, nor does dilute sulfuric acid. Nitric acid and hot sulfuric acid, acting as oxidizing agents, attack copper and form the nitrate and sulfate, respectively. The soluble compounds of copper are poisonous.

**563. Uses of Copper.** For making electrical conductors, copper is used more extensively than any other metal. It finds use for sheathing ships, for making electrotypes, in the manufacture of alloys, for making hot water heater coils, and for roofing, gutters, and flashings.

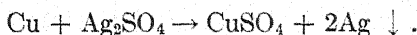
*Brass* is an alloy of copper and zinc; *bronze* is an alloy of copper and tin which may also contain zinc. *German silver* contains copper, zinc, and nickel. All the coins contain some copper, some of them as high as 95%. For hardening gold, copper is much used in making jewelry.

**564. The Compounds of Copper.** In *cuprous oxide*,  $\text{Cu}_2\text{O}$ , copper has a valence of 1; in *cupric oxide*, its valence is 2. The cupric compounds are the more important. Copper oxide is used in rectifiers to change alternating to direct current. No compound of copper is so important as *copper sulfate*,  $\text{CuSO}_4$ , which forms large blue crystals having the formula,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . It is generally known as *blue vitriol*, or *blue-stone*. We have already learned that it is effective in destroying algae and bacteria in city reservoirs. It finds use as a mordant in calico printing, for copper plating and electrotyping, and as a fungicide and insecticide. For spraying fruit trees and grapevines, it is generally used in the form of *Bordeaux mixture*, a preparation made by mixing a solution of copper sulfate with slaked lime. This preparation was first used in the vineyards of France to prevent mildew. It has also been found to be effective for spraying potato vines in efforts to check blight.

## B. SILVER

**565. How Silver Occurs in Nature.** Many ores of copper and lead are silver-bearing. Such ores are so refined that the silver can be recovered. Silver is found free in nature. The compounds, *silver sulfide*,  $\text{Ag}_2\text{S}$ , and *silver chloride*,  $\text{AgCl}$ , are found in nature. The latter is called *horn silver*. It is soft enough to be cut with a knife. When so cut, the surface resembles "horn" in appearance. Like copper, silver was known to the ancients. The United States, Mexico, Canada, and South America are the largest producers of silver.

★ **566. How Silver Is Extracted.** In recovering the silver from the copper refining process, the anode "mud" that is left is screened and then treated with sulfuric acid, which dissolves the silver but not the gold that is present. To the silver sulfate solution that is formed, scrap copper is added to precipitate the silver. The equation follows:



*Parkes' process.* In recovering silver from argentiferous lead ores, the lead ore is roasted and treated as described in Section 582. Then the lead, which contains both silver and gold, is heated in a reverberatory furnace. Such impurities as arsenic and antimony are oxidized and skimmed off the surface of the molten lead. Pieces of zinc are then added to the lead, which is stirred in large kettles. The gold and silver are much more soluble in zinc than they are in lead. Therefore they leave the lead and form an alloy with the zinc. This alloy is lighter than the lead, and it is removed as it floats at the top of the kettle. (See Fig. 324.) When this alloy is heated in a retort, the zinc distills off, and it is condensed for further use. Small quantities of lead that were removed with the zinc alloy are left after the zinc is boiled off. It is separated from the silver and gold by heating the residue left in the retorts in bone-ash or cement *cupels*. In this process of

*cupellation*, part of the lead is oxidized and part is absorbed by the cupel. The silver is then separated from the gold by the use of sulfuric acid.

**567. Properties of Silver.** Silver is a soft, white, lustrous metal. It is very ductile and malleable. Its specific weight is 10.5. Of all the metals, silver is the best conductor of heat and electricity.

Silver is an inactive metal, since it does not oxidize even in moist air. If the air contains traces of sulfur, however,

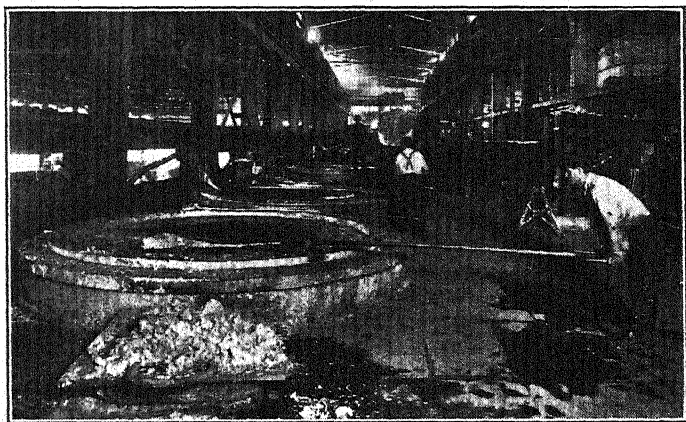


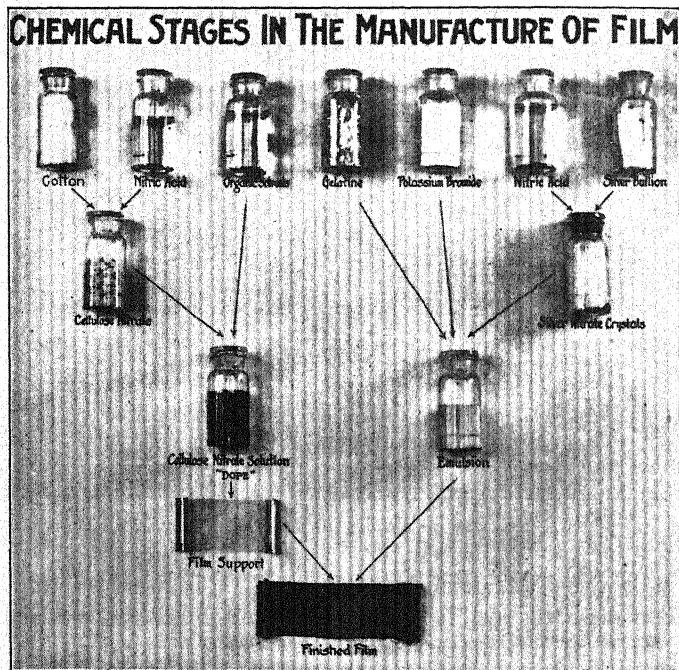
FIG. 324. — Kettles for desilvering lead.

a brownish-black tarnish of *silver sulfide* is readily formed. Silver dissolves readily in nitric acid and in hot concentrated sulfuric. Hydrochloric acid does not attack it, nor does dilute sulfuric acid.

**568. Uses.** Silver is used in jewelry and coins. The United States silver coins contain 90% silver and 10% copper. The British coins contain 92.5% silver. *Sterling silver* is an alloy having the same per cent of silver as the British coins. Large quantities of silver are used for plating tableware. In silvering mirrors, advantage is taken of the fact

that silver compounds are easily reduced, the silver being deposited on the glass as the reduction occurs. Enormous quantities of silver are used in making silver compounds for use in the manufacture of photographic films and plates. (See Fig. 325.)

**569. Silver Compounds.** Silver nitrate,  $\text{AgNO}_3$ , crystallizes in colorless scales. Under the name of *lunar caustic* it



Courtesy of Eastman Kodak Co.

FIG. 325. — The chemicals used in the manufacture of photographic film.

is sometimes used by surgeons for cauterizing abnormal growths, or wounds caused by the bites of animals. Silver nitrate solution used to paint the throat of a smoker is said to create a distaste for tobacco. *Oxidized silver* is made by

dipping silver into a solution of some sulfide, usually that of sodium or ammonium. The name is a misnomer, since the compound formed is *silver sulfide*, and not the oxide. *Silver chloride*,  $\text{AgCl}$ , *silver bromide*,  $\text{AgBr}$ , and *silver iodide*,  $\text{AgI}$ , are all sensitive to light when organic matter is present. The action is one of reduction. Metallic silver is formed. It is finely divided and very dark in color. These compounds are all used in photography. (See Figs. 326 to 331, inclusive.) *Argyrol* is a compound of silver with protein. It finds use in medicine.

**570. The Principles Involved in Photography.** The main steps in the chemistry of photography consist: (1) In preparing the negative; (2) In making the print. In the preparation of the negative there are three important operations: (a) *the exposure*; (b) *developing*; (c) *fixing*. The plate used for making the negative is prepared by covering a glass plate or celluloid film with gelatine containing silver bromide in suspension. This plate is *exposed* to the light just long enough to start the reduction of the silver bromide. It is then treated in a dark room with a *developer*, which consists of rather mild reducing agents, such as hydroquinone or pyrogallol. The developer cannot start the reduction of the *unchanged* silver salt, but it can continue the reduction begun by the action of the light. After the developing process has proceeded far enough, the plate or film is then put into a strong solution of sodium thiosulfate, commonly known as *hypo*. This solution dissolves the unchanged silver salt so the plate will not darken when again exposed to the light. The "hypo" thus serves as a *fixer*. The more intense the light, the more rapidly the reduction occurs. White reflects more light than colored objects; hence white objects make the plate very dark and *vice versa*. For these reasons the plate is now called a *negative*. (See Fig. 332.)

In making the print, a well-sized paper, sensitized in the same manner as the plate, is covered by the negative and

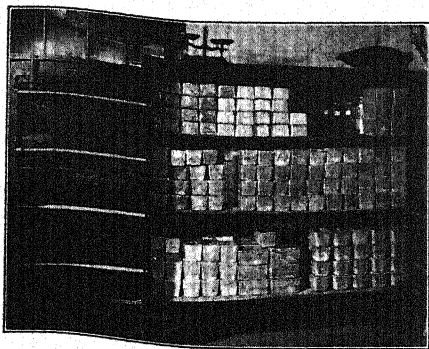


FIG. 326 at the left shows enough silver bullion to last a large manufacturer of photographic films for one week. One-tenth of all the silver mined in the United States is used by one company for making sensitizing films, plates, and print paper. The United States Mint is the only industry that uses so large a supply of silver.

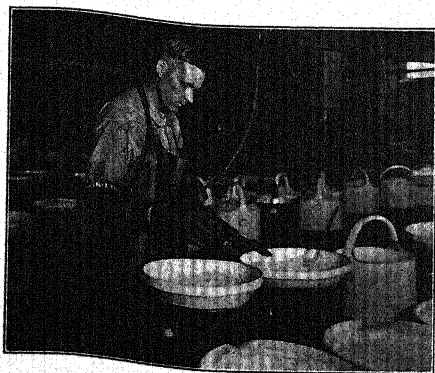


FIG. 327 shows a workman purifying silver nitrate. The silver is dissolved in nitric acid, and the solution of silver nitrate is heated in large evaporating dishes to expel the water. The nitrate that is formed is purified by fractional crystallization. The nitrate of silver is then converted into the chloride, bromide, or the iodide.



FIG. 328 shows the washing and drying of cotton preparatory to the nitrating process. The cotton is then treated with a mixture of nitric acid and sulfuric acid to form cellulose nitrate. A colloidal suspension, from which long rolls of thin films are manufactured, is then produced.



FIG. 329 shows a workman coating the film with an emulsion that is sensitive to light. After the silver nitrate has been converted into silver bromide, a colloidal suspension of this sensitive salt is incorporated with gelatine or protein. Then the cellulose nitrate film is given an even coating of the light-sensitive emulsion.

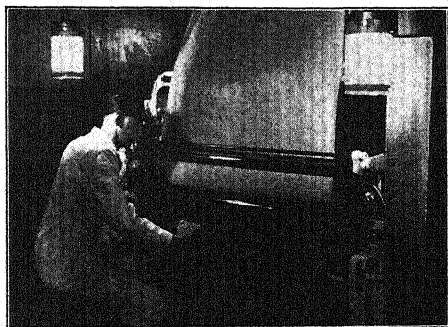
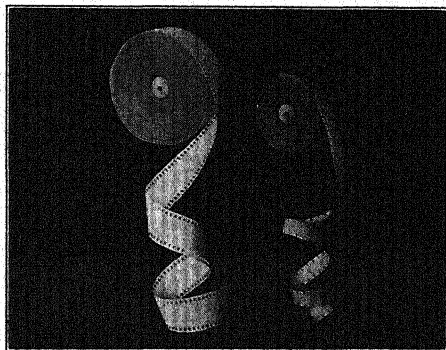


FIG. 330 gives us a view of the machines used to cut the films into strips of the desired width. The work as represented in Figs. 329 and 330 must of course be done in rooms where only red light is used. The films are then wrapped in opaque paper, and are ready for exposure.



FIG. 331 shows rolls of film of different widths. The standard film (for professional use) is 35 mm. wide, and the film for amateur use is 16 mm. wide. Sometimes cellulose acetate is used for making the films instead of the cellulose nitrate, because it is less flammable. Such film may be used without a special booth.





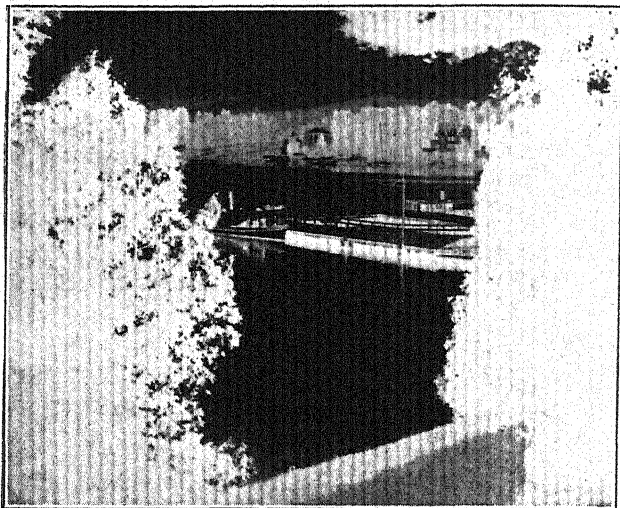


FIG. 332. — A negative plate.



FIG. 333. — A positive print.

then so exposed that the light must pass through the negative. Here the dark part of the negative cuts off the more light and the intensity of reduction is just the reverse from that in the production of the negative, and a positive print is produced. (See Fig. 333.) The print is developed and fixed in the same manner as the plate. It is often *toned* by dipping it into a solution of the salts of gold or platinum. The silver goes into solution, replacing the gold or platinum which is thus deposited on the print in place of part of the silver. Gold gives warmer tones than silver. Platinum produces a purplish color, or even a black. Sometimes the silver is partially oxidized and then converted into a sulfide to produce a sepia print.

### C. GOLD

**571. Occurrence.** We have already seen that gold is obtained from the ores of lead and copper. It is also found *native*, either in fine particles mixed with sand, or in veins of quartz. It can be profitably extracted when the quartz contains only a fraction of an ounce per ton of material.

★ **572. Extraction.** When the gold occurs in *alluvial sand* deposits, hydraulic mining is used. Streams of water directed against the deposits carry away the earthy material through sluices. The heavy gold falls to the bottom where it is retained by riffles. (See Fig. 334.)

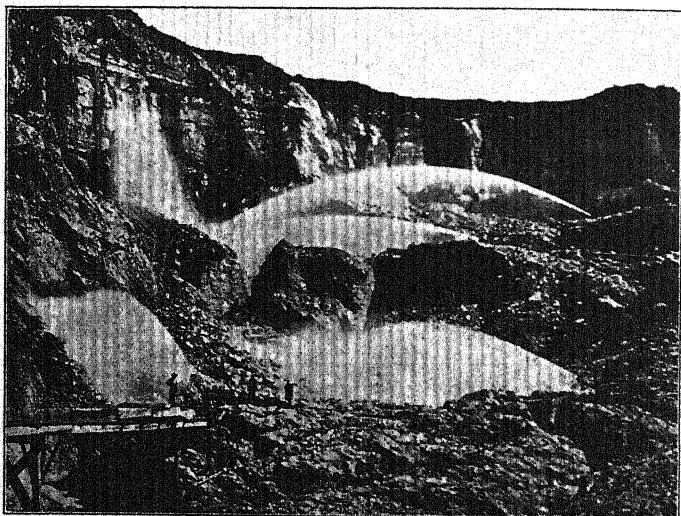
*Gold-bearing quartz ores* are crushed to a fine powder by the use of a stamp mill. As the powder is carried away by running water it comes into contact with mercury, which forms an amalgam with the gold. The gold amalgam is then distilled to recover the mercury.

From certain ores gold is extracted by treating them with moist *chlorine* gas. The gold is dissolved by the chlorine, forming *auric chloride*,  $\text{AuCl}_3$ . Ferrous sulfate serves as a reducing agent to precipitate the gold.

Low-grade ores are treated with *sodium cyanide* in the

presence of air. The gold goes into solution as a double cyanide of sodium and gold, from which the gold can be precipitated by the addition of a metal or by electrolysis.

**573. Properties and Uses of Gold.** Gold is a soft, yellow metal, very ductile and malleable. It has been hammered out into sheets so thin that it would take about 250 of them



*Courtesy Joshua Hendy Iron Works*

FIG. 334. — Streams of water wash down the alluvial gold deposits in hydraulic mining.

to make a sheet as thick as a leaf of paper in this book. Gold is a good conductor of heat and electricity. It is a very heavy metal, its density being 19.3. It is about 7 times as dense as aluminum and nearly twice as dense as silver. Gold does not tarnish when exposed to the air; it is a very inactive metal. No single common acid affects gold, but it dissolves quite readily in aqua regia.

Gold finds use in making coins and jewelry. Since it is too soft to wear well, it is usually alloyed with copper. Its purity

is expressed in *carats*, pure gold being 24 carats fine. Eighteen-carat gold contains 75% gold and 25% copper. Gold coins contain 90% gold.

★ 574. **Compounds of Gold.** In *aurous* compounds gold has a valence of 1; its valence is more often 3, in *auric* compounds. *Auric chloride*,  $\text{AuCl}_3$ , is one of the most important compounds of gold. It is used in photography. A double cyanide of gold and potassium is used in gold plating.

## SUMMARY

The *sulfides* and *carbonates* of copper are important ores. Copper also occurs *native*. The ores of copper are roasted, and then reduced with carbon. Copper is generally refined by electrolysis.

Copper is a heavy, ductile metal used extensively for electrical conductors. It is a self-protective metal. Nitric acid attacks copper readily.

*Copper sulfate* is used in batteries, for copper plating, for water purification, and as a fungicide and insecticide.

Silver is the best conductor of heat and electricity known. It is used in jewelry, in silver coins, and for plating tableware.

Silver salts are sensitive to light. Thus they find use in photography. Two important steps in photography consist: (1) in making the negative; (2) in making the print.

In making a negative there are three operations: (1) the exposure, which starts the reduction of the silver salt; (2) the developing, which continues the reduction; and (3) the fixing, which removes the unchanged silver salts and makes the negative permanent.

The same operations are used in making the print; it is frequently toned by replacing the silver on the print with gold or platinum.

Gold is mined by the *hydraulic* or by the *amalgamation* process. It is often extracted by dissolving the gold with *chlorine* or with *sodium cyanide*.

Gold is a valuable yellow metal. It does not tarnish; hence it is suitable for use in making coins and jewelry. Pure gold is 24 carats fine.

## QUESTIONS

## GROUP A

1. Why is copper not suitable for making cooking utensils?
2. How could scrap iron be used to recover copper from the waste waters of copper mines?
3. How could you tell gold from brass?
4. What is Bordeaux mixture? For what purpose is it used?
5. Why must copper be so highly purified?
6. Why is silver-plated ware more easily scratched than sterling silver?
7. What causes eggs and mustard to tarnish silverware?
8. How would you test for copper and its compounds?
9. What is "oxidized" silver?
10. Why should gold rings not be permitted to come into contact with mercury?
11. How could you make colloidal gold? What use is made of colloidal suspensions in photography?
12. What advantages has copper for use in making screens for doors and windows? What are its disadvantages?
13. Copper-roofed buildings soon acquire a greenish color. What compound formed by weathering gives this color?

## GROUP B

14. If dilute sulfuric acid does not act on copper, explain how copper sulfate can be made by putting copper shot in a lead basket and alternately dipping them into warm dilute sulfuric acid and then suspending them in the air.
15. By the aid of a labeled diagram, outline a method of plating tableware with silver.
16. How is iron separated from copper in the complex copper-iron sulfides?
17. Tarnished silverware may be cleaned by putting it in an aluminum dish containing boiling water and a little baking soda. Explain.
18. Outline the various steps from the time a photographic plate is exposed until the print is finished.

19. How can gold be recovered from gold chloride?
20. Can you give a reason why indelible inks often contain silver salts?
21. Sodium and potassium are both widely distributed, but they are comparatively new metals. On the other hand, copper, silver, and gold were known to the ancients. Explain.
22. How does coin silver differ from "sterling" silver?

## PROBLEMS

## GROUP A

1. What per cent of crystallized copper sulfate is copper?
2. How many pounds of crystallized copper sulfate can be made from 10 lb. of copper?

## GROUP B

3. How many grams of silver and how many grams of bromine are needed to make 500 gm. of silver bromide?
4. How many pounds of copper are needed to displace 40 lb. of silver from a solution of silver sulfate?

## SUPPLEMENTARY PROJECTS

Prepare a report on one of the following topics:

1. How an electrotpe is made.  
Reference: *New International Encyclopedia*.
2. How a mirror is silvered.  
Reference: *Scientific American*, 134:86-9, Feb., 1926.
3. Color photography.  
References: *Literary Digest*, 98:8-9, Aug. 11, 1928.  
LUCKIESH, M., *Color and Its Applications*. D. Van Nostrand.

## CHAPTER 38

### TIN AND LEAD

**575. Introductory.** To some extent, tin and lead resemble carbon and silicon. They have a maximum valence of 4, although tin also has a valence of 2, and lead in its various oxides may be 1, 2, 3, or 4. These elements differ from carbon and silicon, since they both act as metals. In some cases, however, they do act as acids and form salts known as *stannates* and *plumbates*.

#### A. TIN

**576. Where Is Tin Found?** If we read Phœnician history, we learn that the Phœnician sailors braved the terrors of the Black Sea in search for tin. Later they pushed westward to Spain for the same metal, and finally we find that they sailed as far as the islands of the Cassiterides, an old name for the peninsula of Cornwall, England, in their search for *cassiterite*,  $\text{SnO}_2$ , the chief ore of tin. It is commonly called "tin stone," or "stream tin." England has long been a producer of tin, but rich ores have also been found in the East Indies and in Bolivia. Tin is the only common metal that is not produced in quantity in the United States. The Black Hills of Dakota yield small quantities.

★ **577. How Tin Is Extracted.** Although the United States does not mine tin, yet considerable quantities are extracted here. We live so much upon "tin cans" that we are the largest consumers of this metal. From the mines of Bolivia the ore is placed in bags and packed down the Andes Mountains on the backs of llamas; then it is loaded on vessels to



be shipped to the smelters in the United States. The ore is sintered and mixed with carbon to be reduced in the blast furnace. Figure 335 shows the tapping of a blast furnace used for the reduction of the ores of tin. The metal is cast into anodes and refined by electrolysis. (See Fig. 336.)

**578. Properties of Tin.** Tin is a soft, white metal, a little lighter than iron. It has a very low melting point,  $232^{\circ}\text{C}$ . The pure metal is known as *block tin*. It is so malleable that it may be rolled into very thin sheets, known as *tin foil*.

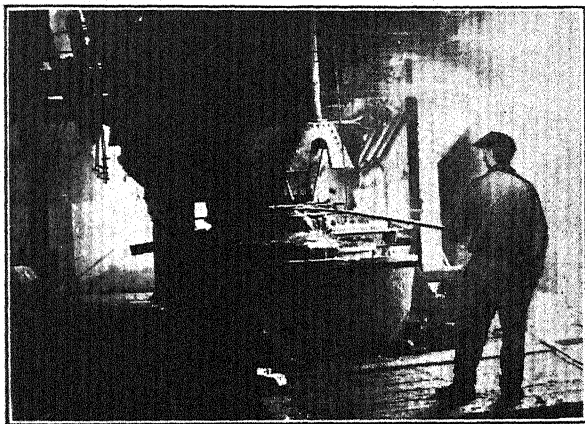


FIG. 335. — Blast furnace for reduction of tin.

Air and water do not act on tin at the ordinary temperature. Dilute acids have little effect on tin, but concentrated acids attack it readily. With hydrochloric acid it forms stannous chloride. Sulfuric acid forms a sulfate of tin. The action of nitric acid on tin is very peculiar. No nitrate of tin is formed, but the tin is oxidized to form *metastannic acid*,  $\text{H}_2\text{SnO}_3$ , a white insoluble compound. In cold climates tin changes to a brittle gray powder. This is an allotropic form of tin. This crumbling of tin in cold weather is sometimes spoken of as "tin disease."

**579. Uses of Tin.** Ordinary *tinware*, or *tin plate*, is made by cleaning sheet iron and dipping it into molten tin. (See Fig. 337.) Such tinned iron is used for making "tin" cans and cooking utensils. Some machines are capable of making as many as 50,000 tin cans an hour. If the coating is thick enough, it protects the iron very well. But we do know that a tin can rusts rapidly under some circumstances. If the tin is scratched away at any one place, the iron will rust even more rapidly than unprotected iron, because the more active of two metals in contact with one another becomes negative with respect

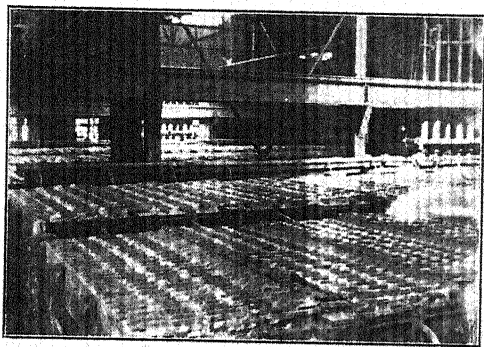


FIG. 336. — Tank house for the electrolysis of tin.

to the less active, and corrosion is accelerated. In reality, the tin and iron form a voltaic cell, in which the tin is positive and the iron is negative. Let us compare this action of tin with that of zinc when the latter is used to protect iron. If the zinc is scraped away from a small spot on a piece of galvanized iron, the surrounding zinc still affords protection for the iron that is exposed. From the replacement table, we find that zinc is negative with respect to iron. Hence we find the spot from which the zinc was removed gradually becoming larger as the zinc goes into solution. For this reason zinc is sometimes called a "sacrificial metal." Tin finds use in making *tin foil*, which is used for wrapping chocolate and other

foods. The cheaper grades sometimes contain lead, but such foil should not be used for wrapping foodstuffs. Pure tin pipes are sometimes used as conduits for slightly acid liquids.

*Solder* is an alloy of tin and lead. Soft solder contains equal amounts of each metal, but a hard solder contains larger quantities of lead. Plumbers use a solder containing 67% of

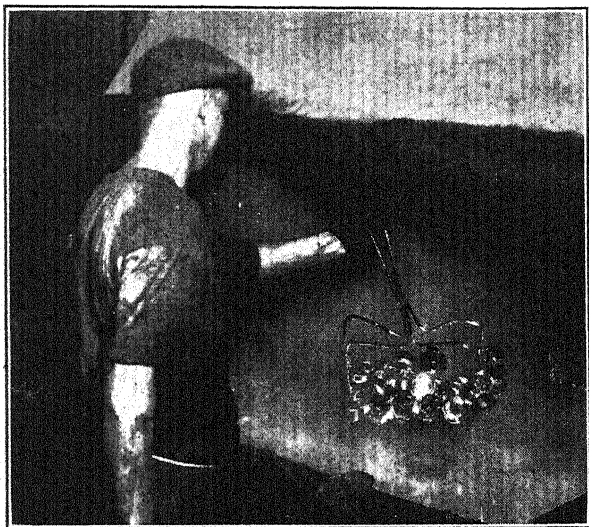
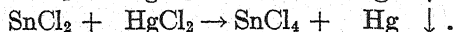
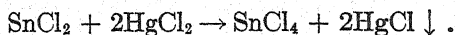


FIG. 337. — The iron is carefully cleaned, dipped into melted tallow, and then into a vat of molten tin in the making of tinware.

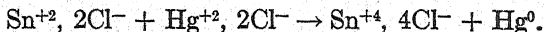
lead for "wiping" joints when installing waste pipes and drains. Such a solder becomes plastic before it becomes a rigid solid, and in this plastic condition it can be used to connect a drain pipe with a sink. Such alloys of tin as *bronze*, *type-metal*, *anti-friction metals*, and *fusible metals* have already been studied.

**580. The Compounds of Tin.** This metal forms two classes of compounds, *stannous* and *stannic*. If we dissolve tin in hydrochloric acid, *stannous chloride*,  $\text{SnCl}_2$ , is formed. It

finds use as a mordant, because it forms brilliant shades with some dye-stuffs. It is used to some extent for weighting silks. When so used, it may hydrolyze in moist climates and form hydrochloric acid, which soon destroys the silk fiber. It is a good reducing agent. An interesting example of oxidation that does not involve a transfer of oxygen occurs when a solution of stannous chloride is added to mercuric chloride. By varying the amounts, we can produce reactions as represented by the following equations:



In each case the mercuric chloride acted as an oxidizing agent and the stannous chloride as a reducing agent. We observe that the tin, which has a valence of 2 in *stannous* chloride, is oxidized to the *stannic* condition, in which the valence of the tin is 4. In the meantime, the mercury in the *mercuric* chloride is reduced to 1 in the *mercurous* chloride, or to zero in the metallic *mercury*. Let us rewrite the second equation to indicate the valence changes:



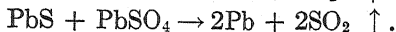
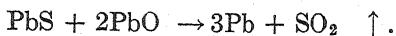
*Stannic sulfide*,  $\text{SnS}_2$ , is used as a yellow pigment under the name of "mosaic gold." *Metastannic acid* is used to strengthen cotton fibers and to render them non-flammable.

## B. LEAD

**581. Where and How Lead Is Found.** By far the most important ore of lead is *galena*, or lead sulfide,  $\text{PbS}$ . It is also known as *galenite*. It occurs as grayish-black crystals, cubical in shape. In the United States lead is found abundantly in Missouri, Illinois, and Colorado. Canada is a large producer of lead, and lead ores are also mined in Mexico.

★ **582. How Is Lead Extracted?** If the ore is free from siliceous matter, it is first roasted at a low temperature in a reverberatory furnace. Such roasting converts part of the lead

sulfide into *lead oxide*,  $\text{PbO}$ , and part of it into *lead sulfate*,  $\text{PbSO}_4$ . Then the temperature is raised and chemical reactions occur between the unchanged lead sulfide and the oxidized products. These changes are represented by the following equations:



Low-grade ores, and those containing silica, are reduced in the blast furnace after being mixed with carbon. Lead may be cast into anodes and purified by electrolysis.

**583. Properties of Lead.** A soft, bluish-white metal, lead is about 11.3 times as dense as water. It is malleable, but not ductile. Lead may be made into wire, however, by forcing the heated metal through a small opening. Lead pipe is made in a similar manner by forcing the metal through a ring-shaped opening. The process is known as *extrusion*.

Lead oxidizes quite rapidly, but the coating is adherent and protects the metal underneath. Hydrochloric acid and sulfuric acid have little effect on lead, but nitric acid acts upon it vigorously. Acetic and other organic acids act readily on lead, and water containing carbon dioxide acts upon it slowly. *As all soluble lead compounds are poisonous*, lead is objectionable for use in making water pipes. Lead salts are especially dangerous even in small quantities as they are not readily excreted, but accumulate in the body. "Painter's colic" is a disease due to chronic lead poisoning.

**584. Uses.** Enormous quantities of lead are used in making white lead paint. Sheet lead is used for lining the chambers of sulfuric acid plants and for the plates of storage batteries. Lead pipe is used as conduits for electrical wires; plumbers also use lead pipe since it is easy to cut, it may be readily bent into any desired shape, and its edges may be readily fused or soldered together to make a seamless joint. Lead foil is used for lining tea chests, and as a substitute for

tin foil. Except for its weight, sheet lead makes excellent roofing material.

Shot is made from lead containing a trace of arsenic. The other alloys of lead, such as solder, type-metal, fusible metals, and antifriction metals, have been studied under other titles.

**585. The Oxides of Lead.** The sub-oxide of lead,  $Pb_2O$ , is formed when lead tarnishes. Three other oxides of lead are important: (1) *Lead monoxide*,  $PbO$ , commonly known as *litharge*, is a yellow powder used in the glass, paint, and varnish industries. (2) *Lead dioxide*,  $PbO_2$ , is a brown powder

that is used as an oxidizing agent. It is formed when storage batteries are charged, and it becomes the positive plate. (3) *Red lead*, or *minium*, is an oxide of lead having the formula  $Pb_3O_4$ . It is used as a red pigment. When it is mixed with linseed oil, it serves as an oxidizing agent and causes the oil to "dry" or harden rapidly.

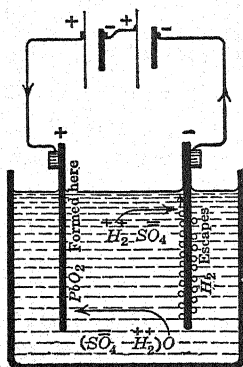


FIG. 338. — Chemistry of storage cell.

**586. The Storage Battery.** In telephone buildings, in power plants, for lighting country homes, and for automobiles, the storage battery finds extensive use. It consists essentially of sheets of lead, carefully insulated from

one another, and suspended in a solution of dilute sulfuric acid. If we pass a current through the acid, electrolysis occurs and water is decomposed just as discussed in Section 27. The oxygen which is liberated at the lead plate which serves as the anode combines with the lead and forms *lead dioxide*. In this manner we use the electric current to store up chemical energy. No electricity is stored. Water is being decomposed during the charging of such a cell, and the *specific weight of the liquid electrolyte increases*. (See Fig. 338.)

We started with two similar plates of lead, but by elec-

trolysis, or the action of the electric current, we made them unlike or dissimilar. *Two unlike plates immersed in a fluid that will act chemically upon one of them form a voltaic cell, and they will produce electrical energy.* As we draw current from such a cell, the oxygen from the lead peroxide formed when the cell was charged combines with hydrogen and forms water. When all the lead peroxide has been reduced again to metallic lead, the cell is *discharged*. (See Fig. 339.) The water that

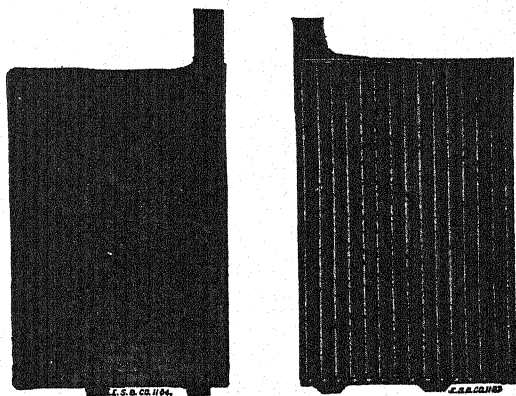
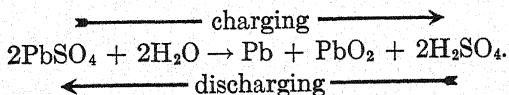


FIG. 339. — Plates for lead storage cell.

is being formed at the same time lowers the specific weight of the electrolyte. A fully charged lead storage battery contains an acid solution whose specific weight is about 1.300. If completely discharged, the specific weight may be as low as 1.100.

The great advantage of the storage cell lies in the fact that it is possible to charge it and recharge it again and again. The chemical action that occurs during the charging and the discharging of a storage battery is represented by the following reversible equation:





**587. How White Lead Is Made.** Several processes are in use for making white lead. The Dutch process has been in use for centuries and yields a very good product. In this

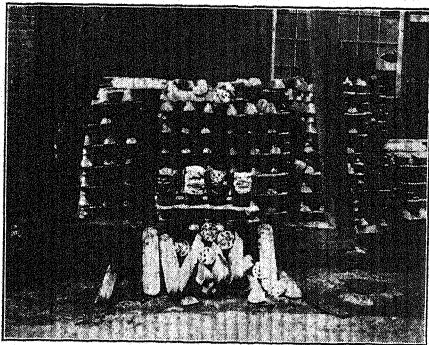


FIG. 340. — Lead ingots from which the buckles are made.

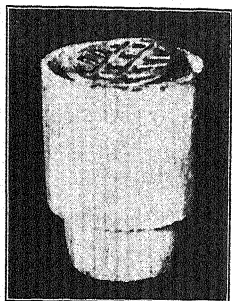


FIG. 341. — An earthenware pot filled with lead "buckles."

process perforated lead discs (Fig. 340), or "buckles," are placed in earthenware pots containing a little dilute acetic acid. (See Fig. 341.)



FIG. 342. — The workman is filling the pots with lead "buckles."

The pots are then placed in rows and covered with stable manure or with spent tan bark. Other tiers of pots are placed on the first ones and covered as before, until a considerable height is reached. (See Fig. 342.) The heat from fermentation vaporizes the

acetic acid which acts on the lead to form a basic lead acetate. Carbon dioxide, which is liberated by the fermentation, changes the acetate into a *basic lead carbonate*. The

process requires 90 days or more. The aim is to produce a white lead having the formula  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , but the product varies to some extent. Figure 343 shows the corroded "buckles" after the tan bark has been removed. White lead is ground very fine with linseed oil and used as a paint base.

In the Carter process melted lead is atomized by a blast of steam and the fine powder is treated with carbon dioxide in a rotating cylinder. The lead is kept moist and acetic acid is sprayed into the cylinder at intervals. It requires about two weeks to make white lead by this process.

★ 588. Other Lead Compounds. *Lead acetate*,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , is a white crystalline solid commonly

known as sugar of lead. Like other *soluble lead compounds*, it is *highly poisonous*. It finds some use as a mordant, and it is sometimes applied externally in cases of ivy poisoning. *Lead chromate*,  $\text{PbCrO}_4$ , is a pigment; it is usually called *chrome yellow*. *Sublimed white lead* is used as a paint base. It is made by roasting galena, which contains some zinc, at a high temperature. The finished product consists of lead oxide, lead sulfate, and zinc oxide. The *arsenate of lead*,  $\text{Pb}_3(\text{AsO}_4)_2$ , is used in large quantities as an insecticide.

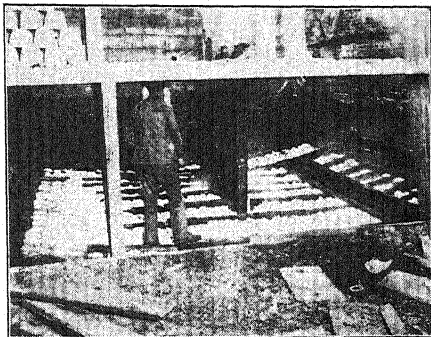


FIG. 343. — Pots of corroded lead.

### C. PAINTS

589. What Constitutes a Paint? A paint consists of: (1) a *paint base*; (2) a *vehicle*. It may also contain some *colored pigment*. A good paint base should be opaque even when it

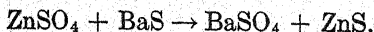
is spread out in thin layers; it should mix readily with the vehicle, which is usually linseed oil, or some other oil that "dries" by forming a tough skin to hold the paint base; it should not become chalky, and it should not peel off; it should work well under the brush; it should be durable; and it should have good covering power.

**590. The Most Used Paint Bases.** 1. *White lead.* For years *white lead* has been used as a paint base, and it is still popular with painters. With the exception of the fact that it becomes chalky with age, white lead answers all the requirements listed in Section 589 remarkably well. But it is poisonous; for that reason its use is forbidden in France. Cases of painter's colic are quite common, and workmen in the factories must submit to a blood examination periodically to determine whether white lead has been absorbed in dangerous quantity. White lead is not suitable for inside use, because it will turn dark or even black when it comes into contact with hydrogen sulfide. Salt air along the seashore causes white lead to deteriorate quickly.

2. *Zinc oxide*, bulk for bulk, does not cover so much surface as does white lead. It is so much lighter, however, that one pound of zinc oxide will cover as much surface as one pound of white lead. Zinc oxide tends to peel, if used alone. It is whiter than white lead, and it does not turn dark when exposed to hydrogen sulfide. Hence it is suitable for use as *inside white*. It is rather interesting to note that each paint base has a tendency to counteract the defects of the other, provided white lead and zinc oxide are mixed in the proper proportions.

3. *Sublimed white lead* is not affected by sulfur vapors nor by the salt air from the sea. It is less poisonous than white lead. It is very durable, and it has good covering power.

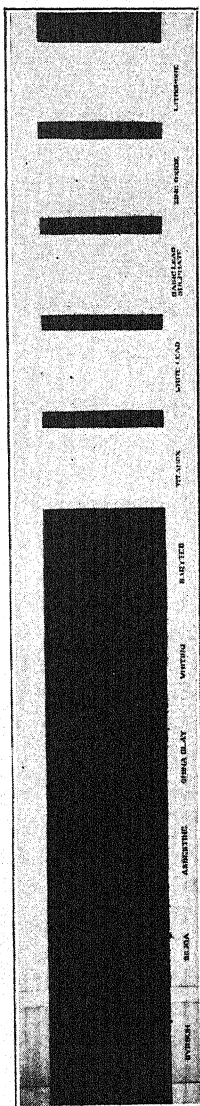
4. *Lithopone* is made by treating zinc sulfate with barium sulfide:



The mixture of the two compounds formed by the above reaction does not make a good paint base. But it may be calcined, plunged into cold water, and then ground in oil to make it a paint base. It is very white and it has good covering power. It is not suitable for outside use, since it darkens when it is exposed to sunlight. It is an excellent paint for inside use and as an undercoat for enamels. It finds use as a filler in making rubber tires.

5. *Titanox* is a paint base that consists of the oxide of titanium,  $\text{TiO}_2$ . It is usually mixed with barium sulfate. It has excellent covering power, and it is durable. Figure 344 along the edge of this page shows the effect of painting a black surface with equal amounts of several different paint bases and fillers. The fillers, gypsum, silica, asbestine, china clay, whiting, and barytes have little covering power when compared to the paint bases, titanox, white lead, basic lead sulfate, zinc oxide, and lithopone.

**591. The Common Vehicles.** *Linseed oil*, obtained from the seeds of flax, is the vehicle most often used in paints. In our study of hydrogen, we learned that some oils solidify when they are treated with hydrogen. Linseed oil is an *unsaturated* compound. (See Section 633.) If oxygen is added to it, a tough, leathery skin is formed. Everyone is familiar with this product, since it forms on the surface of a ready-mixed paint that has stood for a



few days. The formation of such a resin, which is called *linoxyn*, is known as "drying." When linseed oil is mixed with a paint base and the mixture is spread in a thin layer upon some surface, the linseed oil "dries" by taking oxygen from the air, and forms a skin which holds the paint base in place. *Boiled linseed oil* is made by heating the raw linseed oil with oxides of lead or manganese. This treatment makes the oil harden or "dry" more rapidly.

*Chinese wood oil*, or tung oil, is made from the nut of the tung tree which is native to China and Japan. Groves of tung trees have been planted in Florida. It makes an excellent vehicle for use in paints and enamels that must be subjected to severe weather conditions. It forms a hard film, less spongy and porous than that formed by linseed oil.

*Rosin oil* is sometimes used to adulterate linseed oil. It has some drying properties. Some of the "driers" discussed in Section 593 are extensively used by painters. *Fish oils* and the *oil from the soya bean* have been used as vehicles, after proper treatment.

**592. Thinners, or Diluents.** Such substances as turpentine, alcohol, and certain mineral oils (called "painter's spirits") are not vehicles at all. They dry by evaporation, but they do not form a film or skin to hold the paint base or pigment in place. They serve as solvents and thinners or diluents. They should be used only in sufficient quantity to keep the linseed oil from wrinkling as it hardens.

**593. Driers in Paints.** We know that linseed oil hardens by absorbing oxygen from the air. It will harden much more quickly if an oxidizing agent is mixed with the paint to help supply the needed oxygen. The "driers" used in paints are made by heating a part of the oil with the oxides of lead and manganese. They act like catalysts in giving up part of their oxygen to the oil, and subsequently absorbing more oxygen from the air. They are of especial value when the paint contains carbon or some other substance that retards

the oxidation of the linseed oil. Used in excess, "driers" continue to oxidize the linseed oil and finally destroy it.

**594. The Use of Pigments.** The paint bases that have been discussed are all white in color. They form the bulk of nearly all paints. To produce color, a pigment, which is an insoluble substance of high coloring power, is added to the paint base. The pigments include lakes, oxides and sulfides of metals, complex cyanides, and other compounds of widely varying composition. Chromium compounds are especially valuable as pigments.

*Red* pigments include red lead, red ocher, vermilion, and carmine, compounds already studied.

*Blue* pigments include such compounds as Prussian blue, ultramarine, and cobalt blue.

*Yellow* pigments include chrome yellow, yellow ocher, and litharge.

From mixtures of these pigments and others not given here, the various shades may be produced.

**595. Extenders or Fillers.** Many different compounds, known as *fillers*, are sometimes added to paints. At one time they were classed as adulterants, but since they are cheaper and in many cases they make the paint go farther and wear better, they are more properly classed as extenders or fillers. They serve to fill the pores of the wood and make a good surface for repainting. Some large users of paints specify that certain extenders shall be used in paints for their use. The most common fillers include the following: *kaolin*, or *China clay*; *silica*, or powdered sand; *calcium carbonate*, or *whiting*; *calcium sulfate*, or *gypsum*; and *barium sulfate*, or *barytes*.

## SUMMARY

Tin is found in England, the East Indies, and Bolivia. The chief ore is *cassiterite*, or tin stone. Its formula is  $\text{SnO}_2$ . Tin is extracted by reduction with carbon.

Tin is a soft, white, malleable metal. It does not tarnish in the air. Acids act upon it rather readily.

*Tinware* is sheet iron covered with a coating of tin. Tin foil finds considerable use as air-tight wrapping material.

*Solder* contains tin and lead. Other alloys of tin are *bronze*, *type-metal*, and *antifriction metal*.

Tin forms *stannous* and *stannic* compounds. *Stannous chloride* is used as a mordant and for weighting silks.

Lead is a soft, bluish-white metal of high density. Nitric acid and such organic acids as acetic act readily on lead and form salts. *Lead salts are very poisonous*. Epsom salts, or sodium sulfate, may be used as antidotes. When lead is exposed to the air, it tarnishes and forms a protective coating of lead sub-oxide,  $Pb_2O$ .

Lead is used in making paints. It also finds use in making pipe, and as sheet lead. Shot, solder, type-metal, and the fusible alloys contain lead.

*Litharge*,  $PbO$ , and *minium*,  $Pb_3O_4$ , are oxides of lead used in the paint industry. *Lead dioxide*,  $PbO_2$ , is formed on the anode when storage batteries are charged.

The storage battery consists of lead plates immersed in dilute sulfuric acid. Electrical energy is used to form lead dioxide on the positive plate as the battery is being charged. As the battery is being discharged, chemical energy is transformed into electrical energy and the lead dioxide is used up.

*White lead* is a basic lead carbonate that finds use as a paint base. *Sublimed white lead* contains lead sulfate and the oxides of lead and zinc. *Chrome yellow* is lead chromate,  $PbCrO_4$ .

A paint consists of a paint base, mixed with a vehicle. The most common paint bases are: *white lead*; *zinc white*; *sublimed white lead*; *lihopone*; and *titanox*. The most common vehicles are *linseed oil* and *Chinese wood oil*. The latter is used when weather conditions are severe.

A pigment is a highly colored substance sometimes added to a paint base to give it some desired shade or color. An *extender* is a cheap product often added to ready-mixed paints. They are often classed as adulterants, although they may increase the durability of the paint.



QUESTIONS

GROUP A

1. Which makes the better coating for iron, tin or zinc? Give a reason for your answer.
2. Tinware rusts rapidly as soon as a little of the iron is exposed. Explain.
3. What is the chief objection to the use of lead as a roofing material?
4. Compare zinc white and white lead as paint bases.
5. Would you use white lead in a laboratory or a kitchen? Give a reason for your answer.
6. How could you use a solution of lead acetate to test for the presence of hydrogen sulfide in illuminating gas?
7. What is the function of "driers" in paints? Of extenders? Of diluents? Of the vehicle?
8. What is the objection to the use of lead foil for wrapping chewing gum and chocolate?
9. How should you use a hydrometer to determine whether a storage battery is properly charged?
10. What is actually stored in a storage battery? Explain.
11. A mixture of red lead and linseed oil will harden under water. Explain.
12. What are the most important characteristics a good paint base should have?
13. Iron work that is to be painted black is almost always painted with red lead or zinc chromate first. Keeping in mind the fact that black paint probably contains carbon, explain why it should not be applied directly to iron.

GROUP B

14. How could tin be recovered from tin cans?
15. Write the equation representing the reaction between solutions of stannous chloride and auric chloride.
16. Solutions of stannous chloride do not keep well when exposed to the air. What two changes may occur? How does the addition of a little metallic tin and hydrochloric acid aid in preserving such a solution?

17. Can you see any reason why some countries restrict the manufacture and use of white lead?

18. An American chemist won a prize for a method of restoring the color to some valuable paintings that had been darkened by sulfur vapors. He washed the paintings with hydrogen peroxide. Explain the chemical action.

19. What are the advantages and disadvantages of tin plate for roofing?

20. The silk in a shipment to a South American country "cracked" and "split" in a few months. What was the probable reason?

### PROBLEMS

#### GROUP A

1. How many pounds of tin can be obtained from one ton of cassiterite, if the ore is 95% pure?

2. How many pounds of lead can be extracted from 500 lb. of galena? How many pounds of lead acetate can be made from this lead?

#### GROUP B

3. How many pounds of cupric sulfate can be made from 1000 lb. of cuprous sulfide,  $\text{Cu}_2\text{S}$ ?

4. How many pounds of aluminum are required to reduce the iron in 20 lb. of iron oxide,  $\text{Fe}_2\text{O}_3$ , by the thermit process?



## CHAPTER 39

# MANGANESE — CHROMIUM — OTHER ELEMENTS

### Vocabulary

**Polarization.** A defect in a voltaic cell caused by the accumulation of hydrogen bubbles on the positive plate.

**Depolarizer.** A chemical used to remove the hydrogen that causes polarization.

**Impervious.** Non-porous; not easily penetrated.

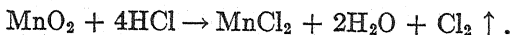
**Photogravure.** A print made from a plate prepared by photographic methods.

### A. MANGANESE

**596. Manganese.** Although several states produce manganese, there is not enough mined in the United States to meet the demand. Rich deposits are found in Brazil and in Russia. There are many minerals that contain manganese, but the chief ore is *pyrolusite*,  $\text{MnO}_2$ . The element can be extracted by reducing its oxide with carbon or aluminum. The metal resembles iron in some respects, but it has a reddish tint. It tarnishes in moist air, and it is readily attacked by the ordinary acids. We have already learned that it finds use in making *spiegeleisen* and *ferromanganese*, and also in the manufacture of extremely hard steel. In its compounds, manganese may act as a base or as an acid. As a base-former, manganese usually has a valence of 2 in *manganous* compounds, and a valence of 3 in *manganic* compounds. As an acid-former, manganese usually has a valence of either 6 or 7.

★ **597. Base-forming Manganese.** In the preparation of oxygen, we used *manganese dioxide*,  $\text{MnO}_2$ , as a catalyst. It

is more often used as an oxidizing agent. We have examples of such use in the paint industry where this compound is used in "driers," in the oxidation of hydrochloric acid to prepare chlorine, or in voltaic cells where it is used as a depolarizer. In voltaic cells the hydrogen produced during the chemical action sometimes accumulates on the positive plate of the cell, and causes a defect known as polarization. The manganese dioxide oxidizes the hydrogen and forms water. There is an interesting valence change when manganese dioxide is used with hydrochloric acid to prepare chlorine:



It is possible that a compound having the formula  $\text{MnCl}_4$  may be formed at first. If so, it breaks down as the reaction proceeds and forms *manganous* chloride,  $\text{MnCl}_2$ . We note that the valence is reduced from 4 to 2. The *manganous* compounds of manganese, in which the manganese has a valence of 2, are more common than the *manganic* compounds in which the manganese has a valence of 3. The *manganous ion* has a pink color.

★ 598. **Acid-forming Manganese.** In the presence of a strong base, it is possible to use an oxidizing agent to convert manganese compounds into *manganates*,  $\text{MnO}_4^-$ , or into *permanganates*,  $\text{MnO}_4^-$ . These compounds are salts of *manganic* and *permanganic* acids respectively. The manganese has valences of 6 and 7 in such compounds. The *manganates* are less stable than the *permanganates*.

*Potassium permanganate*,  $\text{KMnO}_4$ , is the most important compound of acid-forming manganese. It is such a vigorous oxidizing agent that its concentrated solution will oxidize the paper, if we try to filter the solution through ordinary filter paper. Its water solution is a purplish red color, but it becomes colorless when a reducing agent is added. This property makes it useful in making quantitative analyses, such as

those of iron and steel. In an acid solution, potassium permanganate gives up its oxygen to a reducing agent as represented by the following equation:



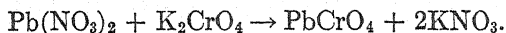
Potassium permanganate finds some use as a disinfectant and an antiseptic. Its dilute solutions may be used for bleaching and in the removal of stains from fabrics. It is used externally in the treatment of ivy poisoning.

### B. CHROMIUM

**599. Chromium**, from the Greek word meaning "color," is obtained from the mineral *chromite*,  $\text{FeCr}_2\text{O}_4$ . This chrome iron ore is found in many localities:— Pennsylvania, Maryland, France, Siberia, Asia Minor, and Africa. The metal may be isolated from this ore by reduction with aluminum, or the alloy *ferrochromium* may be obtained by reduction with carbon. This alloy finds use in making chromium steel. The alloys, *nichrome*, *stainless steel*, *Allegheny metal*, and *stellite*, have been discussed. Chromium is now being extensively used for plating the bright metal parts of automobiles. It is a hard, bluish gray metal that does not tarnish in moist air. It resembles manganese to some extent, especially in its ability to act as either a base-former or an acid-former.

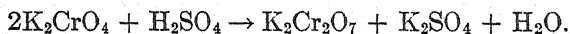
★ **600. Base-forming Chromium.** This element may form *chromous* salts, in which its valence is 2; it may form *chromic* salts, in which chromium has a valence of 3. The chromic salts are analogous to the salts of ferric iron. They are usually green in color, and they find use in making pigments. *Chromic oxide*,  $\text{Cr}_2\text{O}_3$ , is a green powder that is used as a pigment under the name of "chrome green." If solutions of potassium and chromium sulfates are mixed, and the excess water is evaporated, crystals of *chrome alum*,  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , are obtained. This double salt hydrolyzes readily and finds use as a mordant.

★ 601. **Acid-forming Chromium.** *Chromic anhydride*,  $\text{CrO}_3$ , is a red crystalline solid that dissolves in water and forms *chromic acid*,  $\text{H}_2\text{CrO}_4$ . This acid, which is a vigorous oxidizing agent, is not important, but many of its salts are very important compounds. *Potassium chromate*,  $\text{K}_2\text{CrO}_4$ , is a yellow crystalline solid that finds use in the laboratory. When it is added to a solution of some salt of lead, the yellow pigment *lead chromate*,  $\text{PbCrO}_4$ , is precipitated:



*Barium chromate*,  $\text{BaCrO}_4$ , and *zinc chromate*,  $\text{ZnCrO}_4$ , are prepared in a similar manner. Both are yellow pigments that find use in the paint industry. The latter retards the corrosion of iron; hence it finds use in painting structural iron and steel.

If sulfuric acid is added to a solution of potassium chromate, the color of the solution changes from yellow to orange, and *potassium dichromate*,  $\text{K}_2\text{Cr}_2\text{O}_7$ , is formed. The equation follows:



Potassium dichromate, which is an orange-red crystalline compound, is the salt of dichromic acid,  $\text{H}_2\text{Cr}_2\text{O}_7$ . If we write the formula for potassium dichromate as  $\text{K}_2\text{CrO}_4 \cdot \text{CrO}_3$ , the relation between the dichromates and the chromates becomes apparent. The dichromates are excellent oxidizing agents. *A good fluid for cleaning laboratory glassware may be made by adding potassium dichromate crystals to concentrated sulfuric acid.* Such a fluid may be kept and used over and over again. In the presence of reducing agents, the dichromate gives up its oxygen, and sulfates of potassium and chromium are formed. Metallic oxides go into solution in this cleaning fluid, and organic matter is destroyed by oxidation. Potassium dichromate is used in photogravure and half-tone work. If it is mixed with gelatine or asphalt, it forms an insoluble

compound when it is exposed to the light. Potassium dichromate also finds use in tanning light leathers.

**602. Leather** is made from the skins of various animals. The hair is first removed by the action of caustic lime. Then the skin is treated with a dilute acid, which neutralizes the lime and causes the skin to swell decidedly. This part of the process is known as *plumping*. The bark from hemlock and other woods contains *tannin*, a chemical that slowly changes the skin or hide into leather. The product is fairly impervious and it does not putrefy. It is also quite elastic and flexible. Potassium dichromate brings about a similar change in hides by precipitating chromic hydroxide,  $\text{Cr}(\text{OH})_3$ , in the leather. Chrome leather is made more quickly, and it is especially durable. Leather is worked with oil to make it soft and pliable, and to render it less porous. Formaldehyde is used in tanning light leathers to make a soft, washable product.

### C. OTHER ELEMENTS

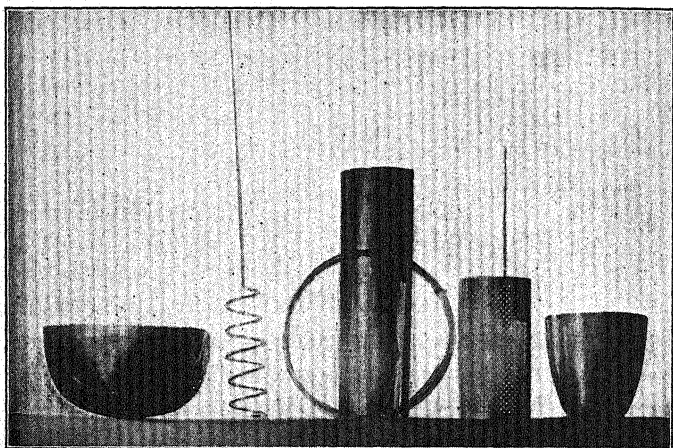
**603. Introductory.** Of the ninety-two elements known, fewer than half of them have been discussed in our study of chemistry. Some of them, too, have been merely mentioned. In this chapter, a few other elements will be briefly discussed. Some of them have only one or two applications. Some of them are so rare that they are costly. Some are difficult to extract from their ores.

**604. Platinum.** This metal usually occurs native. It is mined in Colombia, the Ural Mountains of Russia, and in South Africa. The demand for this metal exceeds the supply, and the price is usually more than that of gold. Some platinum is obtained in the refining of other metals.

Platinum is a soft white metal, which takes a high polish. It is very ductile and malleable. It has a high melting point, about  $1780^\circ \text{C}$ . It is one of the densest metals known. One cubic foot of platinum weighs more than 1300 pounds. It is 21.4 times as dense as water.



**605. Chemical Behavior of Platinum.** Neither dry air nor moist air affects platinum at all. It does not oxidize even when heated white hot. No single acid affects it, but it dissolves slowly in aqua regia and forms orange-colored crystals of *chlorplatinic acid*,  $\text{H}_2\text{PtCl}_6$ . Fused alkalis attack platinum, and so does nascent chlorine. It forms alloys with several metals, especially with such metals as silver and lead.



*Courtesy of Mr. Charles Weller*

FIG. 345. — A group of platinum laboratory utensils.

Hence the salts of such easily reducible metals should not be heated in platinum ware.

**606. The Applications of Platinum.** Since platinum is not easily melted and few chemicals attack it, this metal finds use in the manufacture of such laboratory utensils as crucibles, dishes, forceps, etc. Platinum wire and foil find use in all chemical laboratories. (See Fig. 345.) Considerable quantities of platinum are used in making jewelry. As a catalyst, platinum is useful. When finely divided, it has the ability to occlude or adsorb large quantities of gas. *Rho-*

*dium* and *rhodanized* metals are now being used to some extent as a substitute for platinum.

★ **607. Palladium.** This element resembles platinum in its physical properties and in its ability to adsorb gases. It is less dense than platinum, but considerably harder. It finds some use as a substitute for platinum in jewelry and for laboratory use. It is sometimes alloyed with gold for making laboratory utensils.

**608. Iridium.** This metal also resembles platinum in its chemical behavior. It is hard and it does not tarnish. Gold pens are alloyed with iridium to increase their hardness. An alloy containing 90% platinum and 10% iridium is used for making standard weights and measures.

**609. Tungsten** is a heavy, silver-white metal that has a high melting point, more than 3000° C. The makers of electric bulbs learned how to draw tungsten wire through diamond dies. It is the most satisfactory element yet found for use in making the filaments for incandescent lamps, because its melting point is high, and the metal does not evaporate readily, even at high temperatures. Nearly all the electric bulbs now used for lighting have tungsten filaments. It also finds use in making the targets for X-ray bulbs, for electrical contact points, and in electric resistance furnaces. Its application in the making of high-speed steel has already been mentioned. *Sodium tungstate* is used in fireproofing fabrics.

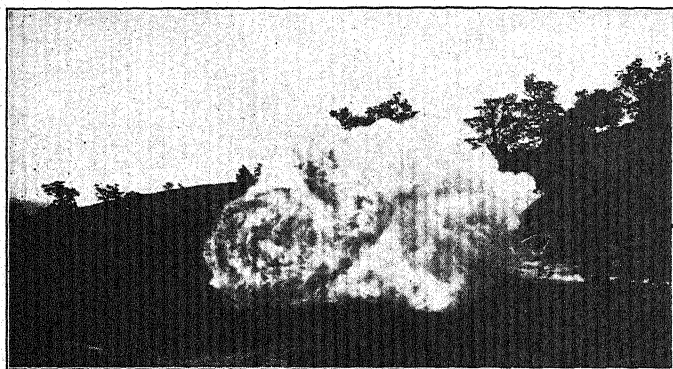
★ **610. Molybdenum** is similar in its properties and uses to tungsten. It has a high melting point. Like tungsten, molybdenum finds use in electric resistance furnaces and in the manufacture of alloy steels for high-speed work.

**611. Vanadium** occurs in minerals found in the Andes Mountains in Peru and in *carnotite*, a radium ore found in the United States. It is a grayish-white metal that has a high melting point. It is used to purify steel and to increase its strength and flexibility. One of the ammonium compounds of vanadium finds use in making aniline black for use in dye-

ing and in producing a permanent black ink. Its oxide is used as a catalyst in the manufacture of sulfuric acid. Some of its compounds find use in coloring glass and as mordants.

★ **612. Uranium.** This element is radio-active. Its oxide is used to produce the greenish-yellow color in glass for making aquaria, lamp shades, and other decorative glassware.

**613. Titanium** serves as a purge in the manufacture of steel. It is especially useful for this purpose, because it combines with both oxygen and nitrogen at the ordinary tem-



Courtesy U.S. Bureau of Mines

FIG. 346. — Such chlorides as those of titanium are used in making clouds of chemical smoke for screening military operations.

perature. It occurs in nature as *rutile* and *titanite*, and in the iron ore *ilmenite*. Its oxide is used in making a paint base, *titanox*. Titanium tetrachloride,  $\text{TiCl}_4$ , finds use in making "smoke screens," since it hydrolyzes readily in moist air. (See Fig. 346.)

★ **614. Zirconium** is a fairly widely distributed element. Its oxide,  $\text{ZrO}_2$ , is an excellent refractory that is made into *zircite* bricks and used for lining furnaces. Its oxide has also been used in making gas mantles.

**615. Selenium**, an element belonging to the sulfur group, occurs in some selenides, but the commercial supply is ob-

tained as a by-product in the refining of copper. It has one unusual property. It is a non-conductor of electricity *in the dark*, but *when it is exposed to light* it becomes a fair conductor. This property makes it useful for making automatic electrical devices, such as burglar alarms and fire alarms. A method of transmitting photographs by electricity is based upon the varying resistance which selenium offers to the passage of the electric current when it is exposed to lights of different intensities. Selenium is used for coloring enamels and for making the red glass used for tail-lights of automobiles.

★ 616. **Thorium and Cerium** are both found in monazite sands. The oxides of these elements glow with a brilliant light when heated to incandescence. For that reason they find use in making Welsbach mantles, which find some use in certain localities. The mantle is woven from artificial silk, dipped into a solution of the *nitrates of thorium and cerium*, and then heated to convert the nitrates into oxides. A film of collodion is applied to protect the fragile mantles during shipment. An alloy of *cerium with iron* is used for making gas-lighters, since such an alloy gives off bright sparks when rubbed on a hard file.

### SUMMARY

The chief ore of manganese is pyrolusite,  $\text{MnO}_2$ . The *dioxide of manganese* is a good oxidizing agent. It finds use in "driers," in voltaic cells, and in the glass industry. Manganese finds use in making alloy steel.

Manganese acts as a base-former. With certain acids it forms *manganous* salts, in which the valence of the manganese is 2; or it may form *manganic* salts, in which the valence of the manganese is 3. In the *manganates* and *permanganates* the element manganese acts as an acid-former. *Potassium permanganate* is a crystalline solid used as an antiseptic, an oxidizing agent, and a bleaching agent.

*Chromium* occurs in nature in the iron mineral *chromite*. The metal finds use in electro-plating, and in the manufacture of stainless steels and tough alloy steels.

As a base-forming element, chromium forms either *chromous* or *chromic* salts. In the *chromates* and *dichromates*, it is an acid-former. Chromium compounds are used as pigments in the paint industry, and as mordants in dyeing. Potassium dichromate is used in making leather, and for half-tone work.

## QUESTIONS

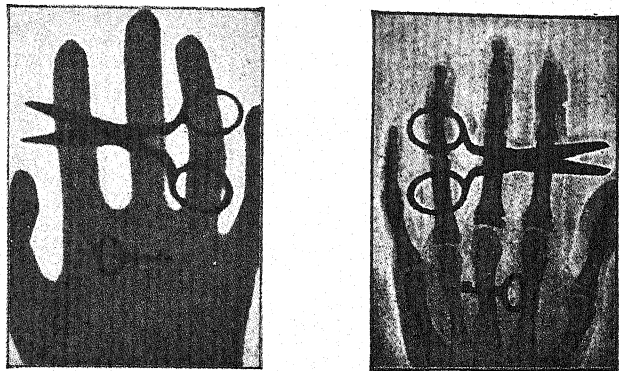
## GROUP A

1. What purpose does spiegeleisen serve in making steel?
2. Name as many oxidizing agents as you can.
3. Name as many reducing agents as you can.
4. Make a list of elements and compounds that we have had which have been used as catalysts.
5. Summarize the properties of platinum that make it suitable for use in making laboratory utensils.
6. Why does platinum occur chiefly in an uncombined state?
7. In what ways may tungsten be substituted for platinum?
8. Name three active metals; three inactive metals.
9. Make a list of metals that do not tarnish in air; of metals that are self-protective; of metals that corrode completely.
10. Name two metals that have a low melting point; three metals that melt at a very high temperature.
11. How are the following stored? 1. Sodium; 2. Hydrofluoric acid; 3. White phosphorus; 4. Gasoline; 5. Quicklime.

## GROUP B

12. Would the change of a chromate to a dichromate be oxidation, reduction, or neither?
13. Make a list of compounds that find use as mordants.
14. How does manganese dioxide serve as a depolarizer in a voltaic cell?
15. For what purposes is a silver crucible superior to one of platinum?
16. What unusual property has selenium? What uses has selenium?
17. Explain how certain elements may act as either acid-forming or base-forming elements.

**619. The Behavior of Radium.** In many respects radium is the most interesting element ever discovered. Its properties are unusual, and it *does* things. Some of its properties are as follows: (1) *It affects a photographic plate*, even when that plate is wrapped up in opaque paper and kept in the dark. It penetrates wood and *thin* sheets of metals. (See Fig. 348.) (2) Radium and its compounds discharge an *electroscope*; they do this by knocking to pieces the air molecules



*Courtesy of Radium Limited U.S.A.*

FIG. 348. — Radiographs. The cut at the left was made by the action of radium rays. The one at the right by the X-rays.

surrounding the electroscope and thus breaking them up into ions. The ions act as conductors and discharge the electroscope. The activity of a sample of radium bromide may be determined by the speed at which it will discharge an electroscope of the type shown in Fig. 349. The rate of discharge is timed with a stop-watch, and the time is compared with that needed by a standard sample to produce a like discharge. In the chemical laboratory, the chemist weighs to 0.0001 gm., or possibly to 0.00001 gm. The electroscope is much more sensitive than the chemical balance for determining the value of radium salts. (3) Radium salts produce *fluorescence* with

certain compounds, just as X-rays do. Hence a very small quantity of radium bromide added to zinc sulfide glows in the dark. Such a mixture is used as a luminous paint for coating the dials of airplane instruments, the hands and dials of

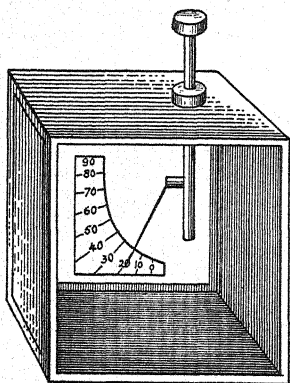


FIG. 349. — An electroscopes suitable for measuring the activity of radium.

require a long time to heal. Those who work with radium are often severely burned by the rays which it produces. (6) In the daytime, the salts of radium resemble common table salt in appearance. In the dark, however they glow with a pale phosphorescence. (7) Radium gives off enough heat every hour to melt 1.5 times its own weight of ice, or about 120 calories per gram. This heat is given off continuously, since radium loses only half its energy in the first 1700 years, one half of what is left the next 1700 years, and so on until practically no energy is left. (8) Radium is rare and expensive. From ores found in Canada and the Belgian Congo, radium salts can be extracted more cheaply

watches, and the sights of guns that are to be used for night firing. (See Fig. 350.) (4) Radium is *active chemically*; it decomposes water, changes oxygen to ozone, and imparts a purple color to glass. It resembles the metals of the calcium family in its chemical behavior.

(5) The *physiological effects* of radium are pronounced. It may destroy the germinating power of seeds, kill bacteria, or even kill small animals. Radium produces frightful burns that re-

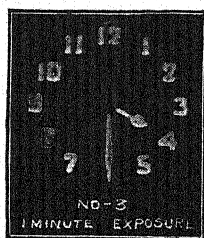


FIG. 350. — Hands of a watch photographed by their radium coating.



than from pitchblende or carnotite ores. The present price is about \$60,000 per gram. *Radium is always found in uranium ores.* In fact, *uranium is the parent of radium.* But in radium ores there is only about 1 part of radium to a little more than 3,000,000 parts of uranium. To produce 1 gram of radium about 500 tons of the ore must be used. Fig-

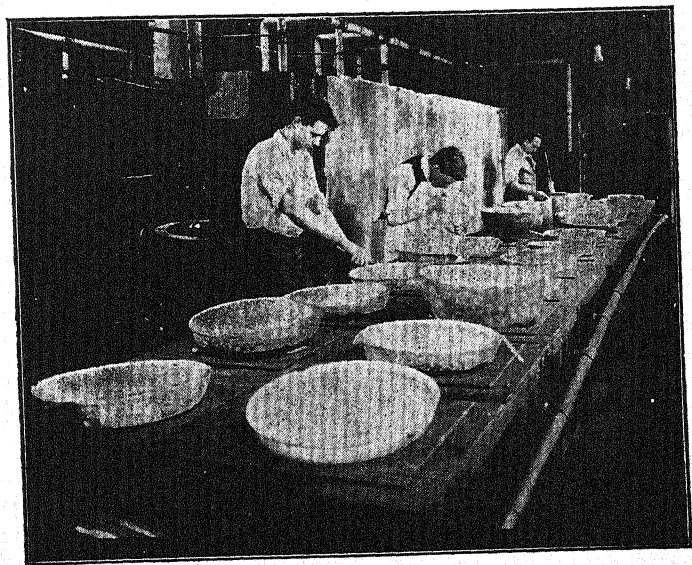


FIG. 351. — Separating radium bromide from barium salts by fractional crystallization.

ure 351 shows the large evaporating dishes used to carry out the seventy-five successive crystallizations needed to separate radium salts from those of barium.

**620. Nature of the Becquerel Rays.** The rays emitted by such elements as radium, thorium, and uranium, known as Becquerel rays, have been carefully studied. In 1899, Ernest Rutherford, then of McGill University, discovered that the Becquerel rays are complex, consisting of three different classes:

1. The  $\alpha$ -rays, or *alpha rays*, are identical with *positively* charged helium atoms. Their mass is nearly four times that of the hydrogen atom; their velocity is from 10,000 to 20,000 miles per second. The alpha rays do not have as great penetrating power as the other rays; a very thin piece of aluminum foil or a thin sheet of paper is sufficient to intercept them. On the other hand, they are very efficient in ionizing air molecules; hence they discharge an electroscope rapidly. Severe radium burns are largely due to the alpha rays.

2. The  $\beta$ -rays, or *beta rays*, are identical with the electron. They consist of negatively charged particles about  $\frac{1}{1840}$  as heavy as the hydrogen atom. Since they travel at a velocity of from 60,000 to 160,000 miles per second, their penetrating power is greater than that of the alpha particles. The *beta ray* seems to be identical with the electrical charge on the negative ion in solution.

3. The  $\gamma$ -rays, or *gamma rays*, appear to have the same nature as X-rays. They are more penetrating than either the alpha or beta rays. The gamma rays are believed to be caused by the impact of beta particles upon the surrounding matter. Figure 352 shows the effect of a powerful magnetic field on the complex Becquerel rays emitted from a small particle of radium. The heavy alpha particles are deflected slightly in one direction; the lighter beta particles are deflected more markedly in the other direction; the gamma rays are not deflected at all.

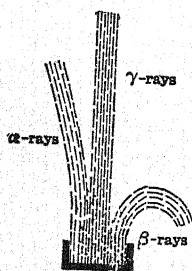


FIG. 352. — Effect of magnet on rays.

By the use of such a magnetic field, Rutherford studied the radiations from radium and learned their nature.

621. **The Uses of Radium.** In Fig. 353 we see girls at work in the laboratory, coating small objects with paint that contains traces of radium. Since radium compounds destroy

bacteria, many attempts have been made to use it in the treatment of certain diseases. The Memorial Hospital in New York has 4 grams of radium bromide from which the gas or emanation produced by its decomposition is collected in small tubes, which are used in treating cancerous growths. (See Fig. 354.) Physicians are not agreed concerning the value of radium for treating such diseases. In some cases it has un-

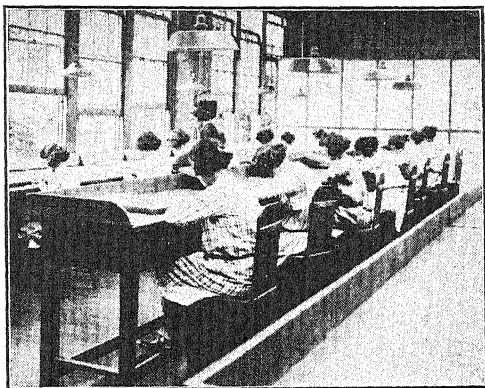


FIG. 353. — Girls at work coating small objects with paint that contains a trace of radium.

doubtedly been successful, but in other cases it appears to have failed miserably.

**622. The Disintegration of the Atom.** Because heat and light appear to be given off continuously from radio-active substances without any apparent loss of weight, it was at first believed that radium is an exception to the law of the conservation of matter and energy. More careful investigation, however, shows that radium does lose its energy slowly.

The question naturally arises, "What is the source of all the energy yielded by radium?" A long series of experiments furnished the answer to this question. *The atoms of radium and other radio-active elements are exploding or disintegrating.*

The alpha and the beta rays are the products of atomic disintegration. *Spontaneously*, certain heavy atoms are breaking down into simpler and lighter atoms. After an average life of about 2500 years, for example, the radium atom explodes. It is 226 times as heavy as the hydrogen atom. When it explodes, it loses an alpha particle, which becomes

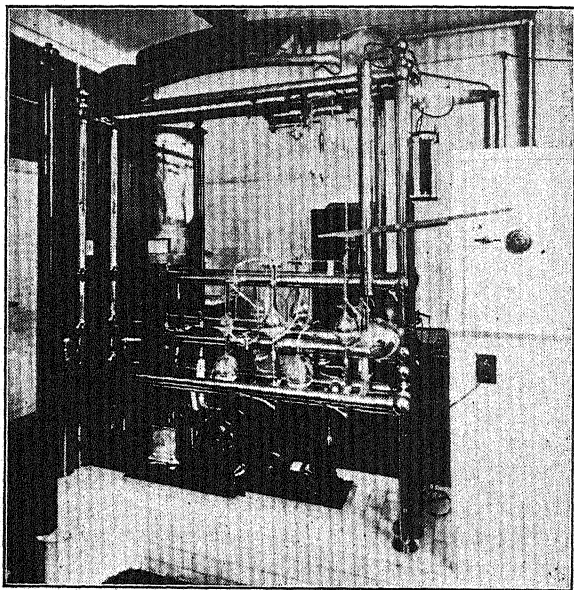


FIG. 354. — Apparatus for collecting radium emanation from radium.

an atom of helium when its electrical charge is neutralized. This helium atom is four times as heavy as the hydrogen atom. The remainder of the atom, which has an atomic weight of 222, is a gas known as *radon*, or *niton*. Thus, two gases, radon and helium, are formed when an atom of radium explodes. The beta particle which is given off is so light that its effect on the total weight is small.

*Radon* loses half its activity in about four days. As it disintegrates, it loses an alpha particle and forms *radium A*, of atomic weight 218. But *radium A* is radio-active and it breaks down forming helium and *radium B*, which has an atomic weight of 214. This disintegrates and forms successively *radium C*, *radium D*, *radium E*, and *radium F*. Figure 355 shows the various steps in the disintegration of the radium atom. When *radium F* loses an alpha particle, it forms an element that has an atomic weight of 206. It appears to be identical with lead. Thus we see that uranium is the parent of radium, but lead is its descendant. Formerly chemists were disposed to scoff at the ideas of the alchemists in their belief in transmutation of one element into another. Now we learn that such *spontaneous transmutation* is going on continuously with certain elements. There is considerable evidence to support the belief that all the atoms are composed entirely of helium and hydrogen.

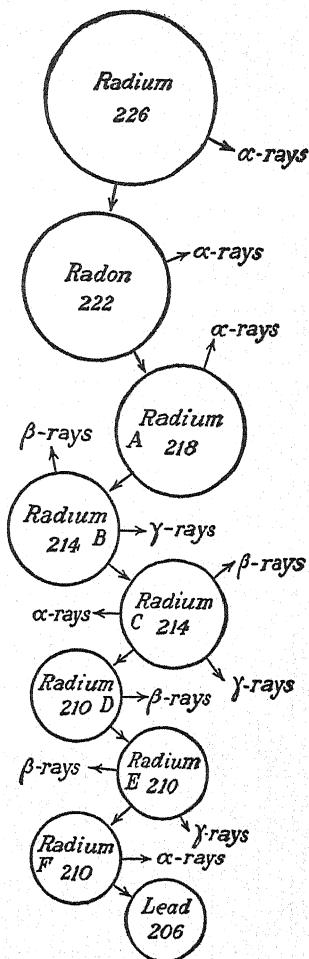


FIG. 355. — Disintegration of radium atom.

**622a. What Is the Modern Picture of the Atom?** Some 130 years ago Dalton proposed his atomic theory, in which the atom is considered a tiny bit of matter, indivisible and

of uniform structure throughout its entire mass. The *facts* and *fundamental principles* of nature are as immutable as the laws of the Medes and Persians, but one who follows the scientific method of approaching problems is forced to change his *theories* when new facts appear. The chemist still finds the atom of Dalton adequate for chemical changes, but it must be discarded in the light of knowledge gained from a study of radio-active substances. The atoms of Rutherford, Lewis-Langmuir, Bohr, and others have appeared in such rapid succession that one wag remarked: "Why worry about the atom? There will be a new one along tomorrow." The Bohr atom is useful in teaching valence, but several new terms used to describe the structure of the atom must be defined.

The nucleus of the atom is believed to contain *protons* and *electrons*. It is compact and dense, but extremely small. It is believed, for example, that if an atom of hydrogen were magnified until its diameter measured some 400 yards, the proton would then be about one inch in diameter, but the electron, some 200 yards distant, would be some 15 to 20 feet in diameter. The proton carries a positive charge of electricity; its mass is only slightly less than that of the hydrogen atom. The electron, which carries a negative charge, is about  $\frac{1}{1840}$  as heavy as the hydrogen atom. It may move at a speed of several hundred miles per second.

In 1932 an American, Carl Anderson, discovered the *positron*, which has the same mass as the electron, but it carries a positive charge. Its existence is too short to give it any great interest from the point of view of the chemist.

In the year 1932, James Chadwick, an Englishman, discovered the *neutron*, a particle which has no electrical charge. It seems to be practically identical with a collapsed hydrogen atom, in which the proton and electron are closely united. Its weight is nearly that of the hydrogen atom. It finds use in the bombardment of atomic nuclei in efforts to disintegrate

atoms. Some stars whose density is one ton per cubic inch are believed to be composed of neutrons.

**623. Can Atomic Energy Be Utilized?** We know that one gram of coal yields about 8000 calories. It is possible to compute the amount of heat energy liberated by one gram of radium when it disintegrates, if we consider that it sets free 120 calories per hour throughout an average life of 2500 years. The total amount is more than 300,000 times as much heat as can be obtained by burning an equal weight of coal.

J. J. Thomson has estimated that the energy stored in one gram of hydrogen equals  $6 \times 10^{11}$  foot pounds. Thus the energy in less than  $\frac{1}{2}$  oz. of hydrogen would be sufficient to lift 10 of our largest battleships (32,000 tons each) higher than the top of Mt. Blanc, over 3.5 miles. Naturally men are fascinated by such enormous quantities of energy, and make efforts to unlock atomic energy and make it available. Rutherford succeeded in disintegrating the nitrogen atom by bombarding it with alpha particles from radio-active substances. The use of the neutron particle seems more hopeful, since it requires a smaller voltage to drive a neutron (neutral) particle into a positively charged nucleus than it does to drive a positively charged alpha particle into the nucleus. Dr. Dunning, of Columbia University, has actually caused such metals as aluminum and silver to become radio-active by bombarding them with neutrons. Possibly at some future time atomic energy may be used in place of coal and gasoline for power purposes.



## CHAPTER 41

### SOME CARBON COMPOUNDS

#### Vocabulary

**Polymer.** A compound having the same percentage composition as another compound; but its molecular weight is different.

**Saponification.** The process of converting fats or esters into soap.

**Enzyme.** An organic compound which is capable of producing by catalysis some chemical change, usually one of hydrolysis.

#### A. SOURCES OF CARBON COMPOUNDS

**624. What Is Meant by Organic Chemistry?** The compounds formed by plants and animals contain carbon and hydrogen, either with or without other elements. Because they are produced by the organs of plants and animals, they were at one time called *organic compounds*, and the name *organic chemistry* was given to that division of chemistry that deals with their study. Elementary carbon and the oxides of carbon, however, are usually studied in *inorganic chemistry*.

Prior to 1828, no one had made any organic compounds in the laboratory. In that year, Wöhler, a German chemist, prepared urea by synthesis. Since that date, a large number of compounds formerly obtained only from plants and animals have been made in the laboratory. For example, indigo was at one time made from plants, but it is made now almost entirely in the dye factories. Since all the so-called organic compounds contain carbon, it seems that this division of chemistry may now more properly be called "The chemistry of the compounds of carbon."

**625. What Is the Source of Carbon Compounds?** We have already learned that certain hydrocarbons and some other carbon compounds are obtained from the *destructive distillation of wood*. Different kinds of wood yield different

products. Reference to Fig. 162 shows us that many such compounds are obtained from the *destructive distillation of coal*. Many hydrocarbons are obtained from *petroleum*. Alcohols are made from fermentation of fruits and grains. The fruits also yield organic acids and sugars. Starch is obtained from the cereals, while fats and oils are obtained from animals, nuts, and seeds. Cellulose comes from cotton and other plant fibers. Scores of compounds of carbon are made in the laboratory. Many of those which have been made are not found in nature at all.

### B. PETROLEUM

**626. What Is Petroleum?** Petroleum is a thick liquid, often of brown or greenish-black color, that is obtained from the earth's crust. It is a mixture of many different hydrocarbons. Although it was discovered in the United States some three hundred years ago, yet the first company organized to drill for petroleum was formed in 1854. Within a few years, oil was being produced in Pennsylvania, West Virginia, and Ohio. Large quantities of oil have been found in Kansas, Oklahoma, Texas, and California.

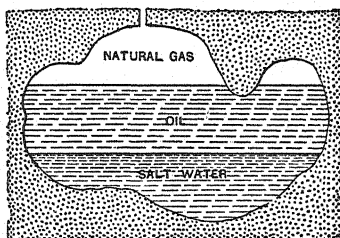


FIG. 356. — Possible condition of an underground oil reservoir.

Petroleum may be found near the surface, or it may lie at a depth of ten thousand or more feet. Holes about 6 to 8 in. in diameter are drilled in the earth until the oil stream or reservoir is reached. (See Fig. 356.) If considerable natural gas is present, the oil may be forced out by the pressure of the gas and form what is known as a "gusher." (See Fig. 357.) Some wells of this kind flow several hundred barrels of oil per day. Some wells produce nothing but natural gas; others

produce nothing but oil; and some wells produce both gas and oil. If the oil does not rise quite to the surface of the earth, pumps are installed to pump the oil to the storage tanks or through pipe lines to the refineries. Some of these pipe lines through which the *crude oil* is pumped are fifteen hundred miles in length. (See Fig. 358.)

**627. How Petroleum Is Refined.** Since petroleum is a mixture of several hydrocarbons that have different boiling

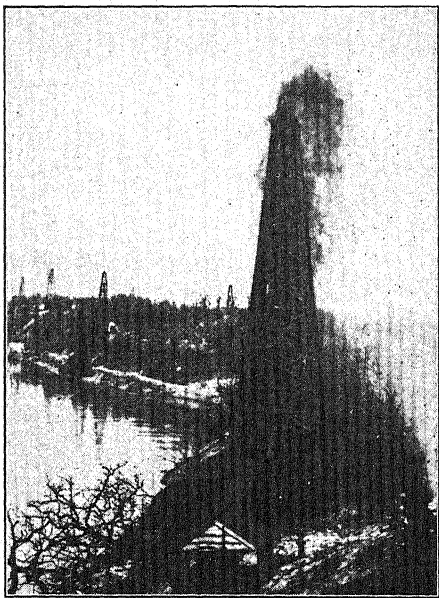
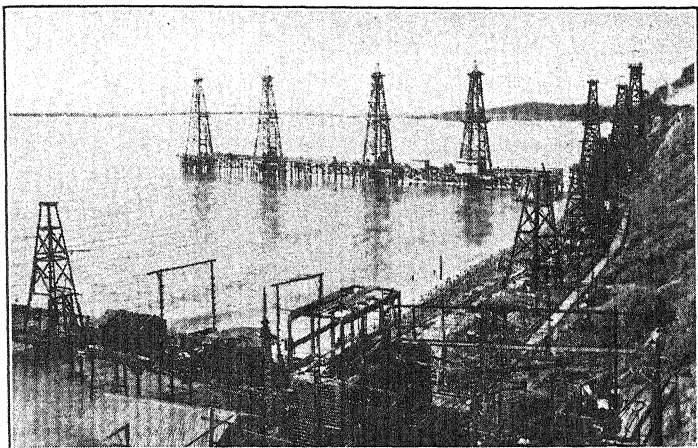


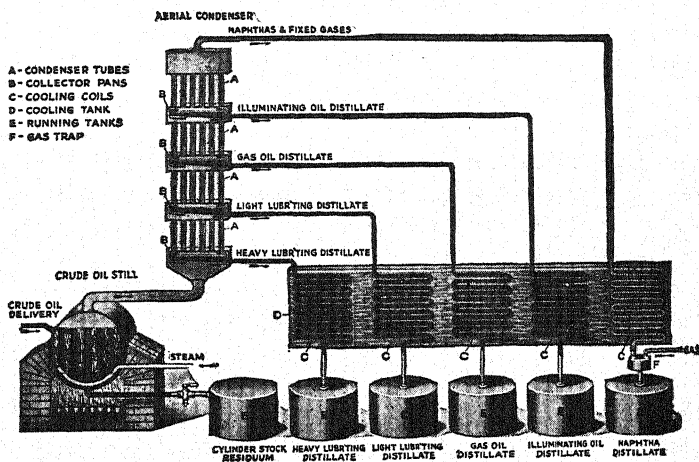
FIG. 357. — A gusher.

points, they can be separated from one another by *fractional distillation*. The most important hydrocarbons found in crude petroleum are *petroleum ether*, *gasoline*, *naphtha*, *benzine*, *kerosene*, *gas oils*, *lubricating oils*, *petroleum jelly*, and *paraffine*. The crude petroleum is heated in a retort, or still, as shown in Fig. 359. As the vapors enter the air condenser,



*Courtesy of N. R. Feasley*

FIG. 358. — Oil derricks in the Pacific Ocean off the coast of California.



*Courtesy of Platt & Washburn Refining Company*

FIG. 359. — Fractional distillation of crude petroleum.

the less volatile products will condense first and flow off into the tank marked "heavy lubricating distillate." Other distillates are separated in the same manner, and from them several separate fractions may be obtained. For purification, these oils are washed with sulfuric acid to char organic matter, with an alkali to neutralize the acid, and then with water.

#### 628. How Refiners Increase the Yield of Gasoline.

1. "*Cracking.*" In the latter part of the nineteenth century kerosene was the most important product obtained from petroleum. It was used for illuminating purposes, but the electric light has almost supplanted it. Before the days of the automobile there was little demand for gasoline. Now the refiner tries in every possible way to increase the amount of gasoline. Let us refer to the table on page 683. We see that the volatile hydrocarbons have low molecular weights. The hydrocarbons that are less volatile have higher molecular weights. For example, *heptane*,  $C_7H_{16}$ , which is present in *gasoline*, boils at  $98^\circ C$ . And *decane*,  $C_{10}H_{22}$ , which may be present in *kerosene*, boils at  $173^\circ C$ . It is difficult to vaporize decane, and it would be hard to start a gas engine using it for fuel. Hence, in the refining of petroleum the chemist conceived the idea of "cracking," or splitting, such heavy molecules into two or more parts in order to increase the amount of volatile fluid. This is exactly what is done in the "cracking process" of refining. The oils are superheated under pressure to "crack" some of the heavier molecules and increase the per cent of gasoline.

2. *Hydrogenation.* A study of the formulas for *heptane* and *decane* shows that the former contains almost 18% of hydrogen and the latter a little more than 15%. This fact furnishes the chemist with another opportunity of increasing the per cent of gasoline obtained from petroleum. By the use of catalysts, it is possible to add hydrogen to some of the molecules of the heavier hydrocarbons, and increase the yield of gasoline. Refining plants for this purpose have been built.

3. *Bergius process*. Several years ago Bergius, a German chemist of Heidelberg, devised a process for converting low grade coal into gasoline and other oils. The powdered coal is mixed with a viscous oil and heated in steel drums under a pressure of 200 atmospheres in the presence of the sulfides of iron, tungsten, and molybdenum as catalysts. When hydrogen is forced into the mixture, it unites with the carbon of the coal to form light liquid hydrocarbons and also some heavy oils suitable for use as lubricants. Plants have been built in England to utilize this process, which it is estimated will yield 30,000,000 gallons of oil from 100,000 tons of coal. The importance of this process needs no emphasis if one considers that our consumption of gasoline amounts to over one billion gallons of gasoline yearly and that geologists calculate that a shortage will begin to develop in from five to eight years.

**629. Uses of Petroleum Products.** The products obtained from petroleum have three important uses: (1) *solvents*; (2) *fuels*; (3) *lubricants*. One of the light liquids, *petroleum ether*, is used as a solvent. *Gasoline*, *naphtha*, and *benzine* are liquids of varying composition. They find some use as solvents, but they are more extensively used as fuels for internal-combustion engines. Painters sometimes use benzine as a substitute for turpentine. *Kerosene* finds use as a fuel and for illuminating purposes. It should have a flash-point of at least 110° F. to make it safe for use in lamps. Many kinds of *lubricating oils* are obtained from petroleum. They range from the light mobile oils, suitable for use with sewing machines, to the heavy engine oils. *Vaseline* and *petrolatum* serve as ointment bases and as lubricants for use as cup-grease and axle-grease. *Paraffin* is used in making candles and chewing gum; it also finds use for insulating electrical apparatus, and in water-proofing paper and fabrics. Those portions of petroleum which are not of value for the purposes already mentioned find use as fuel. Many of our battleships and

destroyers are oil burners. Fuel oil is used in the industries and for heating homes and public buildings. Petroleum coke, the residue left after refining petroleum, is a good fuel.

### C. HYDROCARBONS

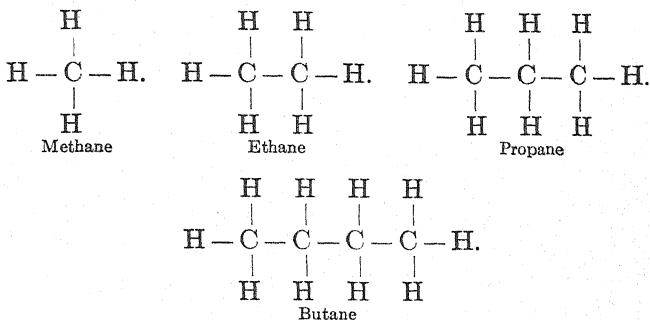
**630. Hydrocarbons.** The 200 or more hydrocarbons known are included in *eight different series*. The *paraffin* or *methane* series and the *benzene* or *benzol* series are the most important. As a rule, each of the other six series has only one important compound in it. As examples of such compounds, we have *ethylene*, *acetylene*, *turpentine*, and *naphthalene*.

**631. What Is an Homologous Series?** Since *hydrocarbons contain nothing but carbon and hydrogen*, the student will be puzzled to know how these two elements can combine to form some 200 hydrocarbons. The valence of carbon is 4, and we would expect to have a compound of the formula  $\text{CH}_4$ . But how are we to explain  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ , or many other formulas that occur in the following table:

Name	Common name	Formula	Melting point	Boiling point
Methane.....	Marsh gas.....	$\text{CH}_4$	.....	Gases { - 164° C. - 90° C. - 37° C. 1° C. 36° C.
Ethane.....	.....	$\text{C}_2\text{H}_6$	.....	
Propane.....	.....	$\text{C}_3\text{H}_8$	.....	
Butane.....	.....	$\text{C}_4\text{H}_{10}$	.....	
Pentane.....	A mixture of pentane and hexane forms <i>petroleum ether</i>	$\text{C}_5\text{H}_{12}$	.....	
Hexane.....	A mixture of hexane and heptane forms <i>gasoline</i>	$\text{C}_6\text{H}_{14}$	.....	Liquids { 71° C. 98° C. 125° C. 150° C. 173° C.
Heptane.....	A mixture of heptane and octane forms <i>naphtha</i>	$\text{C}_7\text{H}_{16}$	.....	
Octane.....	A mixture of octane and nonane forms <i>benzine</i>	$\text{C}_8\text{H}_{18}$	.....	
Nonane.....	.....	$\text{C}_9\text{H}_{20}$	.....	
Decane.....	A mixture of hydrocarbons from decane to hexadecane is <i>kerosene</i>	$\text{C}_{10}\text{H}_{22}$	.....	
Hexadecane.....	.....	$\text{C}_{16}\text{H}_{34}$	18° C.	Solids { 238° C. .....
Hexacontane...	.....	$\text{C}_{60}\text{H}_{122}$	102° C.	



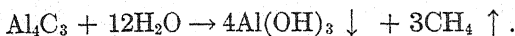
If the series were complete, it would contain sixty compounds. It seems that such a large number of hydrocarbons is possible because *one carbon atom has the rather unusual ability of combining with other carbon atoms*. To show such relationship, we may write *graphic* or *structural* formulas as follows:



An examination of these formulas shows that each one differs from the preceding one by the group  $\text{CH}_2$ . Such a group as  $\text{CH}_2$  is known as a *homolog*. A *series of compounds, each differing from the one that precedes it by such a group, or homolog, is known in chemistry as an homologous series*. In the *methane series* we have  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_5\text{H}_{12}$ , and so on. It is not necessary to memorize such a series, because they correspond to a general formula  $\text{C}_n\text{H}_{2n+2}$ . We simply find the number of hydrogen atoms by multiplying the number of carbon atoms by two, and then adding two to the product. The first compound in the *benzene series* has the formula  $\text{C}_6\text{H}_6$ . Then we have  $\text{C}_7\text{H}_8$  and  $\text{C}_8\text{H}_{10}$ . There are also homologous series of organic acids, alcohols, and aldehydes, in which the  $\text{CH}_2$  group is the homolog.

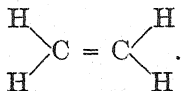
**632. Methane,  $\text{CH}_4$ .** This gas is formed in nature by a decomposition of organic compounds. It forms about 90% of *natural gas*. It is liberated when the mud at the bottom of stagnant pools of water is stirred; hence the name *marsh gas*. It is frequently found in coal mines and called by the

miners *fire damp*. It may be made in the laboratory by the action of aluminum carbide on water:

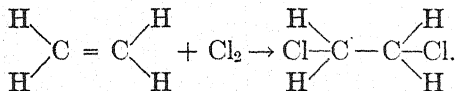


Methane burns with a pale yellow flame. It is used as a fuel.

**633. Ethylene,  $\text{C}_2\text{H}_4$ ,** is the first member of a *second* series of hydrocarbons. Its structural formula is



An organic compound having a *double* bond between two carbon atoms is said to be *unsaturated*, since other elements may be added to it directly to form new compounds. For example, two chlorine atoms may be added directly to ethylene as shown by the following equation:



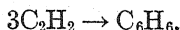
It is impossible to add only one chlorine atom, or more than two. Hence it is obvious that one of the double bonds breaks and links up with the chlorine atoms. Methane has no double bonds and it is impossible to add to it any other atoms. It may form *substitution* compounds, but not *addition* compounds.

Ethylene gas burns with a bright flame. It finds use as an illuminant. During the war, enormous quantities of this gas were used in making *mustard gas*. Ethylene, present in the air even in minute quantities, destroys the chlorophyll or green coloring matter in plants. It finds use in blanching celery, and in the ripening of bananas, oranges, and other citrous fruits. It is now being extensively used as an *anesthetic*. It seems to be more satisfactory in many respects than either chloroform or ether.

**633a. The Octane Number.** Gasoline usually consists of a mixture of heptane,  $C_7H_{16}$ , and iso-octane,  $C_8H_{18}$ . The larger the per cent of heptane, the more likely the gasoline is to cause engine knocks or "ping" when the motor is running. If the ratio of octane to heptane is 75% to 25%, the gasoline is said to have an *octane number* of 75. An octane number of from 68 to 70 is generally high enough for use in most cars, but for a high compression motor, an octane number of 76 is desirable.

**634. Acetylene,  $C_2H_2$ .** We have already learned the preparation, properties, and uses of this gas. Its structural formula,  $H - C \equiv C - H$ , shows that it is an unsaturated compound. It has a *triple* bond between the two carbon atoms. Hence it is possible to add to the molecule two such univalent atoms as chlorine, or even four. Such an atom as copper may be added to acetylene.

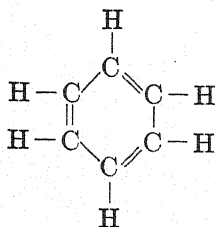
**635. Benzene, or benzol,  $C_6H_6$ .** Benzene, a coal-tar product, must be distinguished from *benzine*, a petroleum product. If we pass acetylene through a hot tube, benzol is formed as represented by the equation:



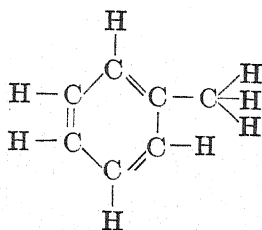
Thus we see that benzol is a *polymer* of acetylene. It has the same percentage composition, but a higher molecular weight. Such *polymerization* seems to be merely "bunching" molecules to form a new compound of different formula. It is common in organic chemistry. *Commercially* benzol is obtained by distilling coal tar. It is a flammable liquid that finds use as a solvent and as the starting point for making many dye-stuffs. Those who work with benzol should be very careful not to inhale its vapor, since it is poisonous. It destroys the red blood cells and produces anemia.

Many chemists tried to work out the structural formula for benzol by the use of the *straight-chain* arrangement shown on page 685. August Kekule, a German chemist, tells us

that he, too, had been working along the same line. In a dream, however, the carbon atoms resolved themselves into a snake, which curled around and took its tail in its mouth. The following day, he worked out the structural ring-formula for benzene which is now generally regarded as correct. In the following formula, we observe that there are three pairs of double bonds:



Benzol, or benzene



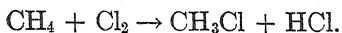
Toluol, or toluene

The formula for toluol shows that it has the benzol ring with a side chain attached to it.

**636. Other Hydrocarbons.** *Toluol*,  $C_7H_8$ , and *xylol*,  $C_8H_{10}$ , are also obtained from coal tar. The former was used for making *tri-nitro-toluol*, or T. N. T., during the World War. Both these compounds find extensive use in the manufacture of dye chemicals. With benzol, they form the *aromatic series* of hydrocarbons. *Naphthalene*,  $C_{10}H_8$ , is a coal-tar compound. It crystallizes in white, shining scales. It is used in "moth-balls" and in the manufacture of drugs and dye-stuffs. *Anthracene*,  $C_{14}H_{10}$ , is also obtained from coal tar. It is used in the preparation of alizarin, a red dye. *Turpentine*,  $C_{10}H_{16}$ , is a hydrocarbon obtained from the long-leaved pine. It is used medicinally and also in the paint and varnish industry. *Asphalt* consists chiefly of a natural mixture of hydrocarbons. The island of Trinidad furnishes large quantities of asphalt, which is used for paving streets. Some of the petroleum found in nature have an asphalt base and others a paraffin base.

D. SUBSTITUTION PRODUCTS OF THE HYDROCARBONS

**637. How Substitution Compounds Are Made.** Although we cannot add atoms directly to the methane molecule, yet it is possible to replace one or more of its hydrogen atoms with elements like the halogens, or with such radicals as OH, NO<sub>2</sub>, NH<sub>2</sub>, etc. For example, *mono-chlor-methane*, CH<sub>3</sub>Cl, may be made by treating methane with chlorine:



This compound is also known as *methyl chloride*. The CH<sub>3</sub> group is an organic radical called *methyl*. It occurs in many organic compounds. If we treat methyl chloride with chlorine, it is possible to substitute more chlorine atoms for hydrogen and produce compounds having the formulas: CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub>. In a similar manner ethane and other hydrocarbons may form *substitution products*. In ethyl chloride, C<sub>2</sub>H<sub>5</sub>Cl, we have the radical C<sub>2</sub>H<sub>5</sub>, which is known as "ethyl." It is present in many organic compounds. It can be made to unite with lead to form *tetra-ethyl lead*, Pb(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, which is a constituent of "ethyl" gasoline. When added to motor fuels it tends to prevent, probably by catalytic action, "motor knocks."

**638. Chloroform, CHCl<sub>3</sub>.** This substitution product of methane is prepared by the action of chlorine on alcohol when an alkali is present. Chloroform is a heavy, oily, sweet-smelling liquid. When inhaled its vapor produces insensibility to pain. Hence it is used as an anesthetic. It finds some use as a solvent.

★ **639. Iodoform, CHI<sub>3</sub>.** If we treat alcohol with iodine in the presence of an alkali, a yellow solid known as iodoform is produced. This reaction serves as a *test for alcohol*, since iodoform has a peculiar, persistent odor. This compound, which has antiseptic properties, was at one time extensively used in hospitals, but it has been largely replaced by other antiseptics.

**640. Carbon Tetrachloride,  $\text{CCl}_4$ .** This colorless compound resembles chloroform to some extent. It is made by treating carbon disulfide with chlorine:

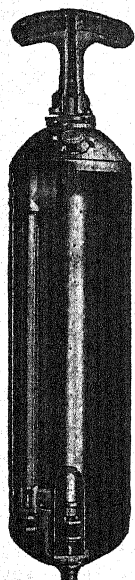
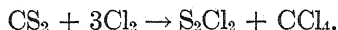


FIG. 360. — Pyrene extinguisher.

On fire-prevention days in our schools we are told that more than a thousand persons are burned to death in a year in the United States from gasoline fires, and that many more are injured. Pupils are urged not to use gasoline for "dry cleaning," but too often they are not told what to use. For removing grease spots and other stains carbon tetrachloride is just as good as gasoline, and its vapor does not burn. Furthermore, its vapor may be used to smother fires. This liquid finds use in small fire extinguishers. It is the liquid used as "pyrene" filler. (See Fig. 360.)

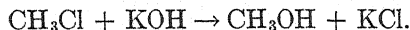
★ **641. Nitrobenzol,  $\text{C}_6\text{H}_5\text{NO}_2$ .** This compound is made by substituting the  $\text{NO}_2$  group for an atom of hydrogen in the benzol molecule. Benzol is treated with a mixture of nitric and sulfuric acids to cause such substitution. This compound is used extensively in making *aniline*.

★ **642. Aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ .** Formerly all the aniline came from the anil plant. Now it is made by treating nitrobenzol with nascent hydrogen. Enormous quantities are used in the *dye industry*. *Toluidine* and *xylidine*, compounds made from toluol and xylol respectively in a manner analogous to the making of aniline, are also used in the dye industry. When we stop to consider that benzol, toluol, xylol, naphthalene, and anthracene are all coal-tar compounds, we can readily understand why this tarry mixture is so important in the dye industry.

## E. ALCOHOLS

**643. What Are the Alcohols?** To the chemist the word "alcohol" applies to any one of a class of compounds that contains an organic radical and one or more OH groups. For example, wood alcohol, which is made by the destructive distillation of wood, has the formula  $\text{CH}_3\text{OH}$ ; ethyl alcohol, made by the fermentation of grains and fruits, has the formula  $\text{C}_2\text{H}_5\text{OH}$ ; and glycerine, which is a by-product in soap manufacture, has the formula  $\text{C}_3\text{H}_5(\text{OH})_3$ . Many alcohols are known to the organic chemist, but only about a half dozen of them are very important industrial compounds.

**644. Wood Alcohol, or Methanol,  $\text{CH}_3\text{OH}$ .** In this compound the group  $\text{CH}_3$ , which is called *methyl*, acts as a radical. Chemically it is known as *methyl alcohol*. To prevent its being mistaken for ethyl alcohol, an attempt is being made to use the name *methanol* for wood alcohol, and *ethanol* for ethyl alcohol. This compound *can* be made by treating methyl chloride with potassium hydroxide:



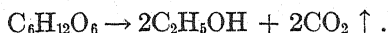
Commercially methanol is prepared either by the distillation of wood or made synthetically by the method described in Section 240.

Pure wood alcohol has rather a pleasant odor, but the commercial product contains impurities that impart to it a disagreeable odor. It is a light liquid, boiling at  $66.7^\circ \text{C}$ . It is very poisonous; cases of poisoning from wood alcohol even when used externally are not uncommon. Its vapor attacks the eyes. When taken internally or inhaled, it often affects the optic nerve, producing partial or total blindness. It is a good fuel, since it burns with a hot, smokeless flame. It also finds use as a solvent of oils, resins, and shellac. It finds use in making denatured alcohol.

**645. Fermentation.** When yeast is added to a dilute



solution containing sugar, chemical action takes place in a short time. Bubbles of the gas, carbon dioxide, are set free and ethyl alcohol,  $C_2H_5OH$ , is produced. The equation follows:



This is an example of one type of *fermentation*, but any *chemical change brought about by the action of some organic body, or ferment, is known as fermentation*. The yeast plants secrete an *enzyme* that acts like a catalyst in changing sugar into ethyl alcohol and carbon dioxide. This type of fermentation is called *vinous fermentation*. Bacteria may act on the alcohol and cause *acetic acid fermentation*. The making of *butyl alcohol*,  $C_4H_9OH$ , the souring of milk, and the decay of foods are all examples of fermentation brought about by the action of molds and bacteria.

**646. Ethyl Alcohol,  $C_2H_5OH$ .** We have learned that this alcohol can be prepared by the action of an enzyme, known as *zymase*, upon fruit juices or dilute sugar solutions. On a large scale it is prepared by the fermentation of such starchy grains as barley, rye, and corn. These grains are first sprouted to change the starch to sugar. The ferment *diastase* present in the grains produces this change. They are then crushed and treated with water and yeast to produce alcoholic fermentation. *Beers* and *wines* produced by this type of fermentation contain from 3% to 10% alcohol. They are known as *fermented liquors*. When the per cent of alcohol in any fermented liquor amounts to about 14%, the fermentation stops because alcohol of that strength renders the ferment inactive.

Liquors of a higher alcoholic content, such as *whisky* and *gin*, are made by distilling fermented liquors. Such distilled liquors may contain from 50% to 80% alcohol. A liquid containing more than 95.5% of alcohol cannot be made by fractional distillation, since a mixture containing 95.5%

alcohol and 4.5% water boils at a temperature slightly lower than 78° C., which is the boiling point of pure *ethyl alcohol*. Hence ordinary commercial alcohol is only 95% alcohol. The last traces of water may be removed by redistilling ordinary alcohol with some dehydrating agent, such as lime. *Absolute alcohol* is water free, or nearly 100% pure.

**647. Properties and Uses of Ethyl Alcohol.** *Ethanol*, or ethyl alcohol, is a colorless liquid that has a peculiar odor and a sharp, biting taste. It has a strong affinity for water, and it mixes with water in all proportions. It boils at 78° C., and its freezing point is - 130.5° C. Alcohol is a good solvent for many plant products. It burns with a nearly colorless blue flame.

When taken internally, alcohol acts as a *narcotic*. In small quantities it deadens the nerves that control the size of the capillaries and thus permits more blood to flow to the surface. The heart beats a little faster and there is a feeling of warmth and vigor that has led to the popular but erroneous belief that alcohol is a stimulant. A little later the heart action becomes slower and the temperature falls below normal. In larger doses, it temporarily paralyzes the nerves. Those nerves that control the action of the heart and lungs are the last to be affected. If enough alcohol is taken to paralyze those nerves, the person dies from alcoholic poisoning. Three ounces in the blood stream at any one time is a lethal dose for the average adult. The *narcotic* effect of alcohol is clearly shown in some experiments carried on in Germany that show that the amount of alcohol contained in a couple of glasses of beer taken daily actually lowers a man's efficiency from 8% to 22%, depending upon his occupation. The amount of alcohol in a pint of beer or an ordinary cocktail is shown by English investigation to double a person's reaction time. Hence an automobile driver who indulges in a couple of glasses of beer will need twice his normal time in which to react in case of an emergency.

Alcohol finds some use as a fuel. It is an excellent solvent of resins and for that reason it finds use in the varnish industry. In pharmacy it is used in extracting from plants certain medicinal constituents. The extracts of bay rum and witch-hazel contain from 15% to 20% alcohol. Tincture of iodine sometimes contains 7% of iodine dissolved in alcohol. Lemon extract should contain at least 5% of lemon oil. To dissolve this oil, an alcoholic solution of about 80% strength is needed. Vanilla extract is made from resins of the vanilla bean which are dissolved in 50% alcohol.

**648. Why Do We Have Denatured Alcohol?** Prior to 1907, every gallon of alcohol legally sold in the United States, whether for use as a beverage or in the industries, paid an internal revenue tax of \$2.10 per gallon. Our makers of drugs, chemicals, etc., could not pay such a tax and compete with manufacturers in many foreign countries that permitted tax-free alcohol to be sold for *industrial* purposes. Hence Congress passed a law in 1906 making exempt from taxation alcohol manufactured for industrial uses. To prevent such alcohol from being used for making beverages, it was "denatured" by the addition of some substances more poisonous than ethanol, or some substance that has a disagreeable odor or taste. Several formulas are in use. One of them, for example, uses 95 gallons of ethanol, 4.5 gallons of methanol, and 0.5 gallon of benzol to make 100 gallons. Denatured alcohol finds use in many industries as a solvent. It is extensively used as an "anti-freeze" solution for automobile radiators.

**649. Butyl Alcohol,  $C_4H_9OH$ .** By the use of special fermentation methods, it is possible to produce butyl alcohol in quantity. The lacquer industry demands a solvent that has a higher boiling point than that of ethanol. Butyl alcohol and its ester, butyl acetate, are extensively used for making lacquers of the cellulose nitrate or cellulose acetate type.

**650. Glycerol,  $C_3H_5(OH)_3$ .** *Glycerine*, or *glycerol*, is a tri-acid alcohol. It is a thick viscid liquid, colorless and odorless, but having a sweet taste. Its most important use is in the manufacture of nitroglycerine. It is also used in some toilet soaps, and medicinally in various lotions. It is used in automobile radiators as an anti-freeze liquid. *Ethylene glycol*,  $C_2H_4(OH)_2$ , is a colorless, syrupy liquid that also finds use as an anti-freeze liquid in automobile radiators.

**651. Phenol,  $C_6H_5OH$ .** Chemically, *phenol* is an alcohol obtained from coal tar, but since it has very feeble acid properties it is commonly known as *carbolic acid*. It is closely related to benzol, as its formula indicates. Pure phenol forms colorless crystals, having a peculiar, persistent odor. It is used in making picric acid for explosives and as a disinfectant. It is now being used with formaldehyde to form such substances as bakelite and condensite which are used for insulating materials, phonograph discs, etc.

The *cresols* are hydroxides of toluol that find extensive use in preserving wood. They are excellent disinfectants. Such derivatives of the coal-tar hydroxides as hexyl-resorcinol are used as disinfectants.

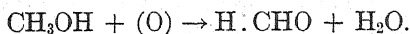
#### F. ETHER

**652. Ether,  $(C_2H_5)_2O$ .** Ether is formed by heating alcohol with sulfuric acid at the proper temperature. Ethers are organic oxides. Ordinary ether, or *ethyl ether*, is a light mobile liquid boiling at about  $35^\circ C$ . It is used to some extent as a solvent, but more extensively as an anesthetic. Nitrated cellulose forms in ether a colloidal suspension. From the jelly-like mass, smokeless powder is formed.

#### G. ALDEHYDES

**653. The Aldehyde Group.** In organic chemistry, the aldehydes comprise a group of compounds that contain an organic radical and the CHO group. For example,

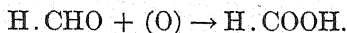
*acetaldehyde* is  $\text{CH}_3\text{.CHO}$ , and *benzaldehyde* has the formula  $\text{C}_6\text{H}_5\text{.CHO}$ . Aldehydes are usually prepared by the partial oxidation of alcohols. If we use a mild oxidizing agent to oxidize wood alcohol, *formaldehyde*,  $\text{H.CHO}$ , is produced:



Formaldehyde is a gas at the ordinary temperature. It is sold under the name of *formalin*, which is a 40% solution of the gas in water. It is an excellent disinfectant. Formalin is often used on seeds before they are planted. Such treatment destroys injurious fungi. Potatoes so treated are less likely to be affected by scab. Formaldehyde finds use in preserving anatomical specimens. With phenol it forms condensite and bakelite.

#### H. ORGANIC ACIDS

**654. Introductory.** Many organic acids and their salts are found in nature. In unripe fruits, in sour milk, and as a result of various types of fermentation, organic acids are found. They all have one or more *carboxyl* ( $\text{COOH}$ ) groups. If we oxidize formaldehyde, formic acid is produced:

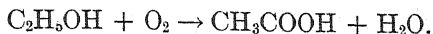


Many organic acids may be made in this manner by oxidizing their corresponding alcohol or aldehyde.

**655. Formic Acid,  $\text{H.COOH}$ .** This acid stands first in an homologous series of acids related to the methane series of hydrocarbons. It is found in nature in red ants, in some bee stings, and in stinging nettles. It is a weak acid chemically, since it does not ionize readily. Physiologically it is active enough to blister the skin. Its salts are called *formates*. They find some use as mordants.

**656. Acetic Acid,  $\text{CH}_3\text{.COOH}$ .** This acid is the second in the homologous series of acids related to the methane series.

It differs from formic acid by the homolog  $\text{CH}_2$ . It may be obtained by the destructive distillation of wood, or it may be made by the action on ethyl alcohol of a ferment known as "mother of vinegar." In this manner the alcohol present in hard cider is slowly changed to acetic acid in the formation of vinegar:



Thus *natural vinegar* is made by two successive fermentations of the juices of fruits, usually from the juice of apples.

- (1) The sugar ferments in the presence of yeasts and forms hard cider, which contains from 5% to 8% of alcohol.
- (2) During the *acetic acid fermentation*, minute organisms change the alcohol to acetic acid. The oxygen needed comes from the air.

In making *artificial vinegar* a dilute solution of alcohol is sprayed into the top of a cylindrical cask filled with beech shavings, which have been treated with vinegar to supply the needed organisms. Air is introduced at the bottom of the cask, and as it rises it meets the alcoholic solution which trickles down over the shavings. While it takes several weeks to make vinegar by the natural process, the *quick artificial process* is complete in a few hours. A good vinegar should contain from 4% to 6% of acetic acid.

**657. Properties and Uses of Acetic Acid.** Acetic acid is a colorless liquid that has almost the same boiling point as water. If it contains less than 0.5% of water, it will crystallize when cooled to  $16^\circ\text{C}$ . This crystalline product is known as *glacial acetic acid*. The acid has a pungent odor. It is a good solvent for organic chemicals. Its salts have the  $(\text{C}_2\text{H}_3\text{O}_2)$  radical. They find use as mordants. The acid itself finds use in making vinegar. With cellulose it forms cellulose acetate, which is used in making "dope" for covering gas bags for dirigibles, and for making the safety motion picture films. It also finds use in the manu-

facture of cellophane, which is so widely used as a wrapping material.

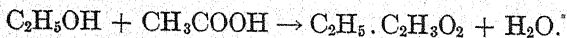
**658. Oxalic Acid,  $(\text{COOH})_2$ .** Chemically this white, crystalline solid acts as a dibasic acid. It has two carboxyl groups. For that reason it may form *oxalates* or *binoxalates*. The acid is an active poison which finds some use in calico printing, as a reducing agent, in bleaching flax and straw, and in cleaning brass and copper. The oxalates are found in such plants as sorrel, oxalis, and rhubarb.

**659. Tartaric Acid,  $(\text{CHOH})_2(\text{COOH})_2$ .** This acid is also dibasic. It is a white crystalline solid. When grape juice ferments, "tartar," or impure potassium acid tartrate, which is insoluble in alcohol, is deposited in the form of crystals. From this "tartar" the acid may be obtained. More often it is purified to be sold as *potassium acid tartrate*,  $\text{KH}(\text{C}_4\text{H}_4\text{O}_6)$ , which is the "cream of tartar" used in making baking powders. *Sodium potassium tartrate*,  $\text{NaK}(\text{C}_4\text{H}_4\text{O}_6)$ , is used in medicine under the name of Rochelle salts.

**660. Citric Acid,  $\text{C}_3\text{H}_4$**   $\begin{matrix} \text{OH} \\ \diagup \\ (\text{COOH})_3 \end{matrix}$  **.** This acid is a white crystalline solid, sometimes called "sour salt." It occurs in such fruits as raspberries, gooseberries, and currants. It is found in lemons, limes, and other citrus fruits. The acid is used in soft drinks. Its magnesium salt is used in medicine.

## I. ETHEREAL SALTS OR ESTERS

**661. What Is an Ester?** We know that an acid and a base unite to form a salt and water. Organic acids unite with alcohols, which have one or more OH groups, and form *esters*, or *ethereal salts*. For example,



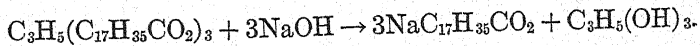
The ethereal salt that is formed is called *ethyl acetate*. It hydrolyzes, since it may really be considered the salt of a



weak acid and an alcohol which acts somewhat like a base. To force the reaction to proceed toward the right, sulfuric acid is used as a dehydrating agent to take up the water that is formed. Esters are also produced when an alcohol unites chemically with an inorganic acid. For example, ethyl nitrite, or sweet spirits of niter, has the formula  $C_2H_5NO_2$ . *Glyceryl nitrate*,  $C_3H_5(NO_3)_3$ , or *nitro-glycerine*, is also an ethereal salt.

**662. Esters in Nature.** Many esters are found in nature in fats and oils. These ethereal salts give to fruits their flavor and they are present in the perfumes of flowers. The name *ethereal salts* is applied to the esters because so many of them have pleasing odors. For example, oil of winter-green is a salt of wood alcohol and salicylic acid known as *methyl salicylate*. It can be made synthetically. Banana oil, which is used as a vehicle for aluminum paint, is an ester known as *amyl acetate*. An ethereal salt made by the interaction of ethyl alcohol and butyric acid has the flavor and odor of pineapple extract. It is ethyl butyrate. This is especially interesting, because butyric acid is present in rancid butter and imparts to it a disagreeable odor and taste. Many fats and oils are glyceryl salts of stearic, palmitic, and oleic acids.

**663. What Is Saponification?** The word *saponification* means "soap-making." If we treat *stearin*, which is the glyceryl salt of stearic acid, with a strong base like sodium hydroxide, sodium stearate or soap is formed and glycerine or glycerol is obtained as a by-product. The equation follows:



*Saponification may be defined as the process of converting fats or oils into soaps by treating them with a strong base.* More broadly, it includes the hydrolysis of all esters. *Stearin* for use in making soaps is obtained from beef or mutton

tallow. *Palmitin*, an ester formed from palmitic acid,  $C_{15}H_{31}COOH$  is found in palm oil. It also finds use in making some kinds of soap. *Olein* is a glyceryl salt of oleic acid,  $C_{17}H_{33}COOH$ , which forms a considerable proportion of lard, olive oil, and cottonseed oil. *Soap* is usually a mixture of the sodium salts of the organic acids mentioned in this

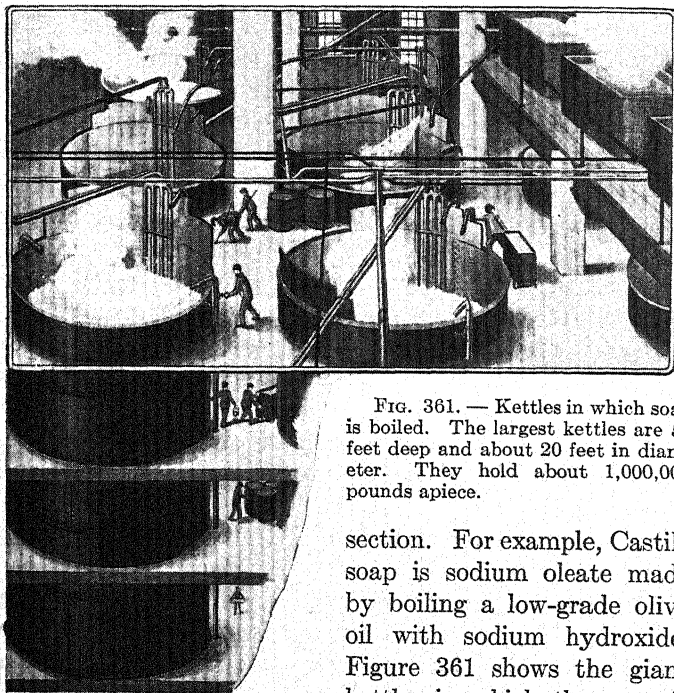


FIG. 361. — Kettles in which soap is boiled. The largest kettles are 50 feet deep and about 20 feet in diameter. They hold about 1,000,000 pounds apiece.

section. For example, Castile soap is sodium oleate made by boiling a low-grade olive oil with sodium hydroxide. Figure 361 shows the giant kettles in which the soap is

boiled. The soap is put through crutching machines (Fig. 362), and then run into molds to solidify. It is then cut into bars, by means of steel wires. Figure 363 shows the first cutting, and the strips ready for the final cutting are shown in Fig. 364.

*Soft soaps* and *liquid soaps* are usually made by using

potassium hydroxide instead of sodium hydroxide to saponify the fats. Shaving soaps are often made by saponifying the fats or oils with a mixture of sodium and potassium hydroxide. We have already learned that calcium and magnesium salts present in hard waters will form a precipitate when soap is added to these waters. Both "lime soap" and "magnesium soap" are insoluble, and no suds can be produced until enough soap has been added to precipitate all the calcium and magnesium present in the water. Some soaps that will lather in hard water, or in sea water, are made from cocoanut oil. These *marine soaps*, or hard-water soaps, contain considerable water. Glycerine is obtained as a by-product in the soap industry.

**664. Fillers and Adulterants.** In the manufacture of soap, some water is incorporated with it. The soap is then

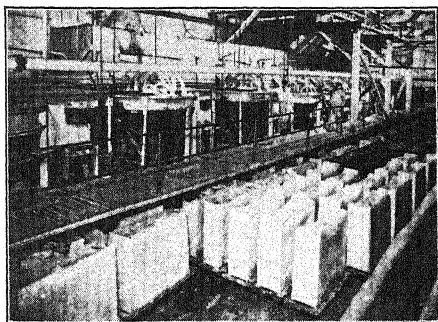
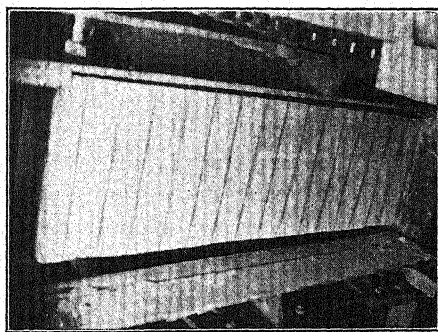


FIG. 362. — The crutching machines are shown in the background. In the foreground are large blocks of soap of about 1200 lb. each.



*Courtesy of The Proctor and Gamble Co.*

FIG. 363. — The steel wires cut the soap into strips.

dried to give it the proper hardness and prevent its dissolving too rapidly. A hard soap should not contain more than 25% of water. *Rosin* is nearly always added to a laundry soap since it increases its lathering power. As it aids in the cleansing process, rosin should be classed as a filler rather than as an adulterant. *Sodium silicate* is added as a filler

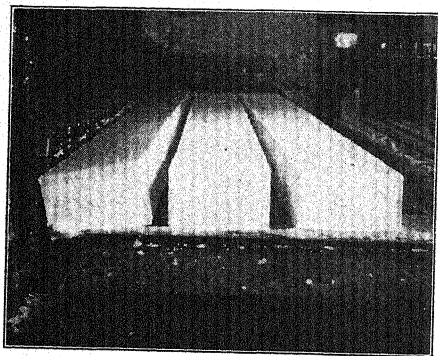


FIG. 364. — The strips of soap are ready for the final cutting. The wires are strung at the right.

in some soaps. Its cleansing properties are slight, and it is injurious to certain fabrics; hence it is sometimes classed as an adulterant. A laundry soap usually contains a slight excess of the base to aid in removing grease or oil from the fabrics. A toilet

soap should not contain free alkali as it will cause the skin to chap or crack.

**665. Cleaning and Laundering.** Dirt may usually be readily removed from the clothing by the mechanical action of water unless grease or oil is present. In such a case the grease sticks to the fiber and the dirt which adheres to it cannot be removed since the binding material is insoluble in water. Soap is water-soluble and it owes its cleansing power to its ability to form an emulsion with fats and oils. The minute fat globules which are held in suspension by the soap solution are easily carried away by the agitation of the water. Dust particles adsorbed on the surface of the bubbles of the soap are also removed in the same manner.

Wool and silk are usually "dry cleaned," since they are likely to be injured by the action of soap and water. In the

“dry cleaning” process some substance like gasoline, benzol, or carbon tetrachloride, is used to dissolve the grease. It may then be absorbed by the use of blotting paper, or with such powders as French chalk or fuller’s earth. Carbon tetrachloride is one of the safest solvents to use since its vapor does not form explosive mixtures with air.

**666. Special Soaps and Scouring Powders.** The *floating soaps* are made by beating air into the soap while it is still liquid. *Transparent soaps* frequently contain glycerine. They may also be made by dissolving the soap in alcohol. Dyes and perfumes are generally added to toilet soaps. The various *medicated soaps* are made by adding to them some substance of supposed medicinal value. *Powdered soaps* are made by grinding a dry, hard soap to a fine powder. If such a soap is to be used in the laundry, sodium carbonate is usually added. *Naphtha soaps* contain a small per cent of naphtha.

*Scouring powders* are generally mixtures of powdered soap, sodium carbonate, and such gritty substances as powdered sand or pumice stone. Many of them contain from 80% to 90% of insoluble matter.

**667. Butter — Oleomargarine.** Butter is an animal fat obtained from milk. The federal law requires that butter shall contain at least 82.5% fat and not more than 16% water. These fats are mainly olein, stearin, and palmitin, but the flavor of butter is largely due to an ester of butyric acid and the presence of small quantities of ethereal salts of capric, caproic, and caprylic acids. Certain bacteria cause butter to ferment or become rancid, the disagreeable odor in such event being due to the formation of the acids from the last four esters mentioned. Butyric acid has an unpleasant odor and taste. Capric acid is present in limburger cheese. As these acids are volatile, such butter may be *renovated* by melting the fat and blowing air through the molten fat for several hours. Such butter is also called *process butter*.

*Oleomargarine* is a butter substitute. It is made from neutral lard, beef fat, cottonseed oil, and palm oil. It is cheaper than butter and is considered just as nutritious. Few persons can tell the difference between butter and oleomargarine by the taste alone. Nut margarine is made from peanut oil and cocoanut oil.

*Butterine* is made by adding a certain per cent of butter to oleomargarine. It is sometimes churned with sweet milk to improve its flavor.

### SUMMARY

*Organic* chemistry is known as the chemistry of the compounds of carbon.

Carbon compounds are obtained by the *destructive distillation* of wood and coal, from the *fractional distillation* of petroleum, and from various plants and animals.

A *hydrocarbon* is a compound containing hydrogen and carbon only. More than two hundred are known. They are used extensively as fuels and solvents. Methane, acetylene, benzol, gasoline, kerosene, vaseline, paraffin, naphthalene, and turpentine are all common examples of hydrocarbons.

Certain elements or groups of elements may be substituted for one or more of the hydrogen atoms in a hydrocarbon. Chloroform, iodoform, carbon tetrachloride, and aniline are important *substitution products* of hydrocarbons.

*Fermentation* is a chemical change produced by the action of a living organism or an enzyme.

The *alcohols* are organic compounds consisting of an organic radical and at least one OH group. Ordinary alcohol is made by the fermentation of sugar. Methyl alcohol, glycerol, and phenol are also important alcohols.

An *ether* is an oxide of organic radicals. Ethyl ether is the most common, being used as an anesthetic.

*Aldehydes* have the CHO group. Formaldehyde is the most common aldehyde. It finds use as a disinfectant and preservative.

*Organic acids* have the carboxyl (COOH) group. Acetic acid occurs in vinegar. Tartaric acid finds use in baking powder.

*Esters* are salts of alcohols and acids. They include animal and vegetable fats and oils, fruit flavors, perfumes, nitroglycerine, etc. Butter and oleomargarine are mixtures of esters or ethereal salts.

*Saponification* is the process by which fats and oils are converted into soap by boiling them with a strong base.

## QUESTIONS

## GROUP A

1. What do you understand by an homologous series? Does the relation appear to hold in the same manner in organic acids?
2. Why is petroleum such an important substance from an industrial standpoint?
3. What is the advantage of using structural formulas in organic chemistry?
4. At one time coal tar was thrown away as waste material. Why is it so valuable at the present time?
5. Is wood alcohol suitable to use as an alcohol rub? Give a reason for your answer.
6. Why is alcohol so important in pharmacy?
7. Why does baking soda relieve the pain from bee stings?
8. Name some common fillers used in soap. Should they be classed as adulterants?
9. State the advantages and disadvantages of using a soap that contains free alkali.

## GROUP B

10. If you were given a substance containing carbon 92.3%, and hydrogen 7.7%, how could you tell whether it was acetylene or benzol vapor?
11. Name one very important part that sulfuric acid plays in organic chemistry. Illustrate, using at least three different cases.
12. Would it be possible to produce formic acid by starting with methane? If so, name the different steps in the process.
13. Why does not a mixture of gasoline and water make as good a cleansing solution as soap and water?



14. Castile soap is often mottled by putting into it ferrous sulfate. This produces green spots. Why do they become red when exposed to the air?

15. Write a 300-word essay on the topic, "What shall we do when petroleum sources begin to fail?"

16. Explain why a person who has taken a cocktail is an unsafe driver.

## CHAPTER 42

### OTHER CARBON COMPOUNDS

#### Vocabulary

**Isomer.** A compound that has the same percentage composition and the same molecular weight as another compound.

**Exudation.** A discharge of juice or gum, as from a pore or incision.

**Cordage.** Ropes or cords.

**Suppurate.** To form pus or matter.

**Aseptic.** Free from the germs that cause pus, or decay.

#### A. CARBOHYDRATES

**668. What Are Carbohydrates?** The hydrocarbons contain carbon and hydrogen only, but the *carbohydrates* contain carbon, hydrogen, and *oxygen*. In nearly all cases, the hydrogen and oxygen are present in the ratio of 2 to 1, the same as in water. This group of compounds includes the various sugars, starch, cellulose, and dextrine.

**669. Many Sugars Are Known.** Of the various sugars *glucose*, *fructose*, *maltose*, *sucrose*, and *lactose* are the most important. *Cane sugar*, *beet sugar*, and *maple sugar* all contain sucrose, which has the formula  $C_{12}H_{22}O_{11}$ . From the chemical point of view, these sugars are all alike. Maple sugar contains some flavoring material that gives it a different taste from beet sugar or cane sugar. The latter two are indistinguishable.

Cane sugar is made by squeezing the juice from sugar cane as the stalks are passed between rollers. It is then clarified by precipitating some of the impurities and filtering the liquid through boneblack. To avoid scorching the sugar and to facilitate evaporation, the syrup is heated in vacuum pans while it is being concentrated. (See Fig. 365.)

Liquids boil at lower temperatures when the atmospheric pressure is reduced, and they evaporate faster. The "mother liquor" left after the crystals of sugar have been removed is known as *molasses*. Pure sugar crystals have a natural yellow tint. A slight amount of some blue pigment is some-

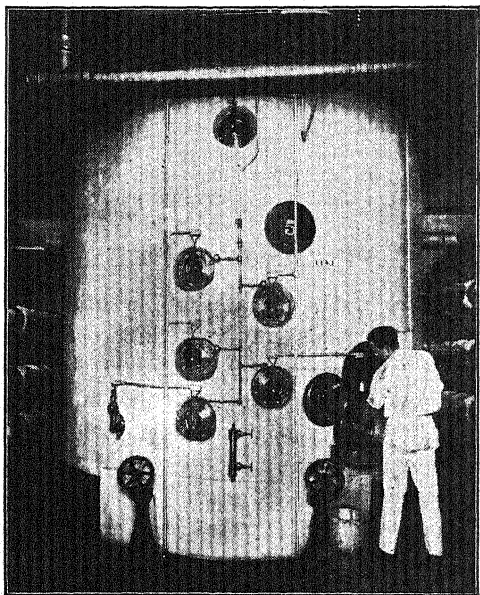
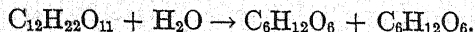


FIG. 365. — Vacuum pan for making granulated sugar.

times added to neutralize this yellow color. Beet sugar is made from beets in a similar manner.

If sucrose is heated to  $210^{\circ}\text{C}$ ., *caramel* is formed. It finds use as a flavoring material in candy and ice cream and as a coloring material. If we add an acid to sucrose and heat it to about  $70^{\circ}\text{C}$ ., the sucrose is converted into two sugars, *dextrose* and *levulose*. The equation follows:



This process is known as *inversion*, and a mixture of the two sugars is called *invert sugar*. The reaction is not reversible. This seems rather peculiar, since it is generally easy to dehydrate a compound by the action of an acid. It will mean a fortune for the one who learns how to make sucrose from invert sugar, for invert sugar can be made from starch, which is a cheap product. Invert sugar is not crystalline, but it is a sticky substance. If we wish to make pulled candy, we add vinegar, which contains an acid, to cane sugar in order to convert it into the sticky invert sugar.

**670. Milk Sugar or Lactose,  $C_{12}H_{22}O_{11} \cdot H_2O$ .** Lactose has the same composition as cane sugar, but it contains water of crystallization. About 5% of cow's milk is milk sugar. It is useful as a food, and it finds extensive use in medicine for making pills or for coating them. Lactic acid bacteria are always present in milk. They act upon lactose and produce a fermentation which converts the lactose into lactic acid, which is present in *sour milk*. Grade A milk contains fewer lactic acid bacteria than does Grade B; hence the latter will sour more quickly.

**671. Maltose,  $C_{12}H_{22}O_{11}$ .** Malt is made by sprouting grains of barley in water and then drying them. The barley grains contain the enzyme *diastase* which converts some of the starch present in the grains into maltose, a very sweet sugar similar to lactose. This sugar is supposed to be very easily digested.

**672. Dextrose or Grape Sugar,  $C_6H_{12}O_6$ .** This compound is often called *grape sugar* or *glucose*. It is found in nature in grapes, in various kinds of fruits, and in honey. Pure *grape sugar* is a white, crystalline solid. It is about three-fifths as sweet as cane sugar. We have learned that it can be made by the inversion of sucrose. It is prepared commercially in large quantities by heating starch with very dilute hydrochloric acid. The acid is then neutralized with

sodium bicarbonate. Dextrose is usually marketed in the form known as glucose, which is a thick syrupy liquid that contains both dextrose and dextrine. Large quantities of glucose are used in making candy, in molasses, and in jams and jellies. The starches and sugars which we eat are converted into glucose by a ferment present in the pancreatic juice. It is a highly concentrated food, and it is not injurious. The only possible objection to its use arises when it is sold as a substitute for cane sugar at the same price as sugar itself.

**673.** Levulose,  $C_6H_{12}O_6$ . *Fructose* or *levulose* is found in many fruits. It is formed in equal quantities with glucose during the inversion of sucrose. The student will observe that it has the same formula as dextrose. In fact, there are known to the chemist eighteen different sugars that have this formula. *Two compounds that have the same percentage composition and the same molecular weight are said to be isomeric.* Levulose is an *isomer* of dextrose. The origin and significance of the names of these sugars afford an interesting side-trip in *physical chemistry*.

If we could see the end of a beam of light, we would see the various rays of which it is composed vibrating to and fro in all directions. Certain

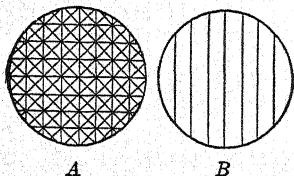


FIG. 366. — A. Possible appearance of end of beam of light. B. Of polarized light.

crystals, such as tourmaline, permit light to pass through them, but they stop all the rays except those vibrating in a *single plane*. Such light is said to be *polarized*. (See Fig. 366.) If a plane of polarized light, coming from a tourmaline crystal for

example, enters a dextrose solution, the *plane is twisted toward the right*. Such a sugar is said to be dextro-rotatory. The Latin word *dexter* means "toward the right." Hence the name "dextrose" for this sugar. The Latin word *laevus*

means "left." *Levulose* is so named because it twists the plane of polarized light to the left.

674. The Source of Starch and Its Properties. The formula for starch is written  $(C_6H_{10}O_5)_n$ . Its simplest formula can be found by the method given in Section 121. But it cannot be vaporized and it is insoluble. Therefore its correct formula cannot be found, because it is impossible to determine the value of  $n$ . Starch is manufactured by the leaves of green plants, and usually stored by the plant in its seeds, its roots, or its stem. Most of the starch made in the

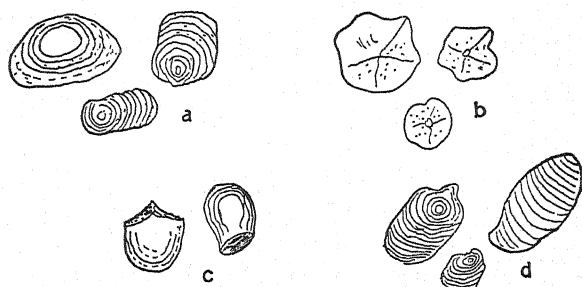


FIG. 367. — Starch grains from various plants.

United States comes from corn, but potato starch is common in Europe. Rice starch is also made in quantities. Starch is made up of granules which vary in appearance. By the aid of the microscope, it is possible to tell from what source the starch was obtained. (See Fig. 367.)

Starch is insoluble in water, but when starch is heated with water, the granules burst, and the *altered* starch forms a colloidal suspension. If only a little water is used, a kind of transparent jelly known as starch paste is formed. In the laundry, starch is used in the form of a dilute paste. When cold starch is used, the fabric is dipped into a suspension of starch granules in water. It is probable that the heat from the iron produces altered starch when the fabric is ironed.

With iodine, starch yields a blue-black color. This color reaction serves as a test for either iodine or starch.

As a food-stuff, starch produces heat and energy. It finds use in the laundry and also as a sizing and filling material. Large quantities of starch are used in making glucose and dextrine. Nitric acid interacts with starch and forms *nitro-starch*, a compound that is a powerful explosive.

**675. Dextrine,  $C_6H_{10}O_5$ .** When starch is heated, or when it is treated with a dilute acid, some dextrine is formed. It is also produced by the action on starch of saliva, diastase, or one of the ferments in the pancreatic juice. Dextrine is a sticky substance used as a substitute for gum arabic in calico printing and as an adhesive for postage stamps and envelopes. It is sometimes added to inks to make them adhere to the paper. Mucilage contains dextrine.

**676. Pectin** is a complex carbohydrate which forms with cellulose a compound known as pecto-cellulose. When certain fruits are boiled with water this compound hydrolyzes and forms pectic acid. This acid and its salts form a jelly when cooled. Fruits which do not contain a pectin compound capable of being changed to pectic acid will not "jell." Pectin is not present in overripe fruits. Too long a boiling decomposes pectic acid present in sour fruits and prevents their forming jellies. Commercial products containing pectin are now sold for use in making jellies.

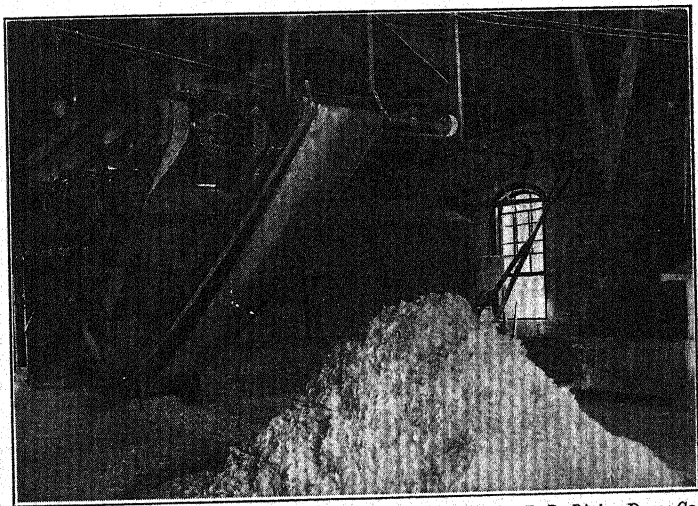
**677. Cellulose,  $(C_6H_{10}O_5)_x$ .** Cellulose may be considered the framework of all woody plants. It has the same formula as starch, but undoubtedly it has a different molecular weight. Cotton and linen fibers are nearly pure cellulose. Wood is largely made up of cellulose, and the cell walls of various plant tissues are composed of cellulose. Like starch, cellulose decomposes if we try to volatilize it, and it resembles starch from the fact that it is insoluble in ordinary reagents. In zinc chloride or in an ammoniacal solution of copper oxide, cellulose forms a colloidal suspen-





*Courtesy of B. D. Rising Paper Co.*

FIG. 368. — Sorting paper rags.



*Courtesy of B. D. Rising Paper Co.*

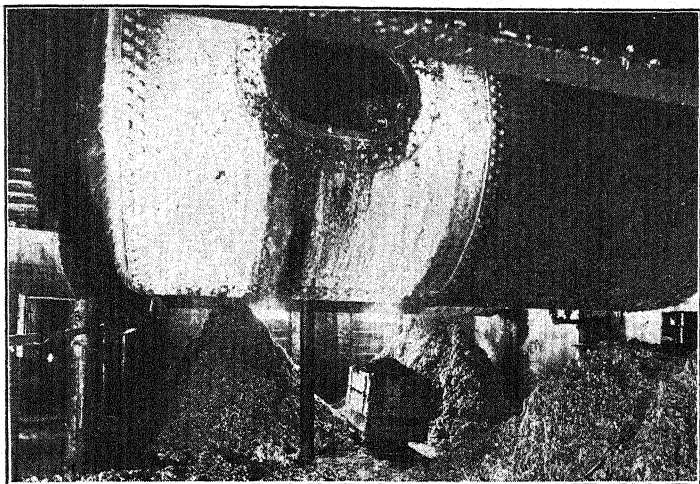
FIG. 369. — Rags cut and dusted ready for boiling.

sion. We have already learned that nitric acid interacts with cellulose to form several different nitrates of cellulose. These cellulose nitrates are used for making smokeless powder, in making collodion and celluloid, in the manufacture of lacquers, and for making so-called "artificial silk." *Parchment paper* is made by the action of concentrated sulfuric acid on cellulose.

## B. THE PAPER INDUSTRY

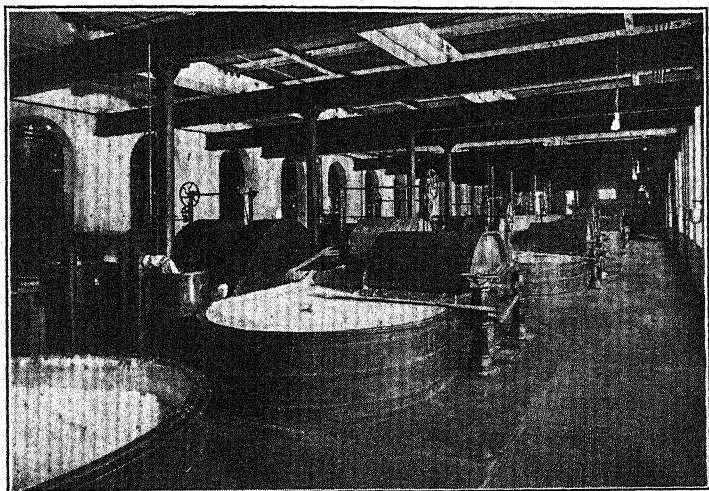
**678. What Is Paper?** The filter paper used in the laboratory is composed almost entirely of cellulose. Such large quantities of paper are used every year that the demand for cellulose for this industry is ever-increasing. Such raw materials as spruce logs, linen and cotton rags are used to supply the cellulose for paper. But our forests are diminishing and other sources of cellulose are being sought. Theoretically any woody plant will supply cellulose for paper, but in some cases the fibers are so short that they do not form a strong mat. It is estimated that some 120,000,000 tons of cornstalks are produced annually in the United States. A plant was built at Danville, Illinois, for the purpose of making paper from cornstalks. Chemists have also experimented with such agricultural wastes as straw and cotton stalks in their efforts to make paper and other useful products.

In making paper from wood, the blocks of wood are first shredded by means of revolving stones, and then treated with some reagent such as sodium hydroxide to dissolve the gummy substances and leave nearly pure cellulose. A better and stronger pulp is made by treatment of the fibers with calcium bisulfite,  $\text{Ca}(\text{HSO}_3)_2$ . If a white paper is desired, some bleaching agent such as sulfur dioxide or chlorine is used. When rags are used they are sorted, and then cut to pieces and dusted before boiling. (See Figs. 368 and 369.) The boiler shown in Fig. 370 is capable of handling about 12,000 pounds of rags at one time. Lime and soda are



*Courtesy of B. D. Rising Paper Co.*

FIG. 370. — A boiler in which 12,000 pounds of rags are boiled at one time.



*Courtesy of B. D. Rising Paper Co.*

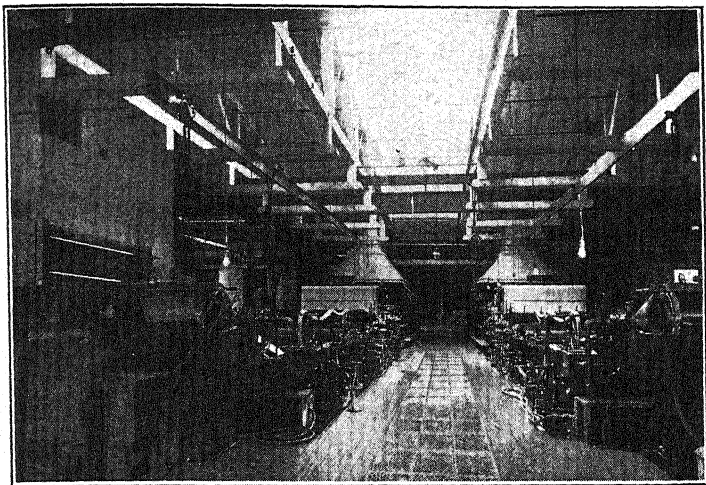
FIG. 371. — The beaters which convert the rags into pulp.

used during the boiling to remove the color and certain impurities. The boiling is continued for several hours. In the further treatment of either rags or wood fiber, the mass is converted into pulp by being run through knives placed on rollers. Figure 371 shows one of the beaters for making pulp. The mass of cellulose is run between the revolving knives and a set of knives on the bed-plate. From the beaters the pulp, which is suspended in water, is run onto screens to form a mat of fibers. (See Fig. 372.) From the screens this mat of fibers passes through rollers which dry it and press it to form paper. Figure 373 shows the finishing rolls of a paper-making machine.

To increase the weight of paper such loading materials as clay, calcium sulfate, and barium sulfate are often added. They give body to the paper and make it less transparent. If the weighting does not exceed 10%, it is not considered an adulterant, although in some papers the weighting material may comprise 30% of the total weight of the finished product. Paper which is to be used with ordinary ink must be sized to close the pores of the paper and keep the ink from spreading by capillary action. Rosin dissolved in sodium hydroxide and then precipitated with aluminum sulfate is often used for sizing. High-grade papers are sometimes sized with gelatine.

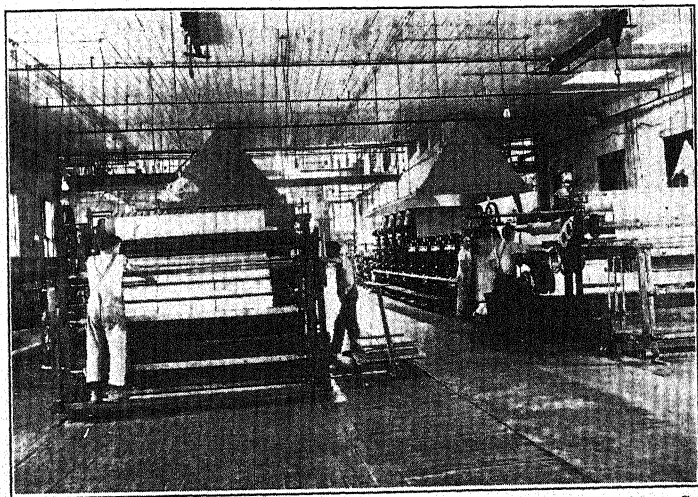
### C. TEXTILES

**679. The Textile Fibers.** Several different kinds of fibers are used extensively in the textile industry. *Silk* and *wool* are animal fibers that contain nitrogen in addition to carbon, hydrogen, and oxygen. Wool also contains sulfur. *Linen* and *cotton* are nearly pure cellulose. The compound microscope furnishes the best method of identifying the different kinds of fibers. (See Fig. 374.) Under the microscope, wool appears scaly; the cotton fibers are flat and twisted; the



*Courtesy of B. D. Rising Paper Co.*

FIG. 372. — Wet end of a Fourdrinier paper machine.



*Courtesy of B. D. Rising Paper Co.*

FIG. 373. — The cutter end of a Fourdrinier paper machine.

linen fibers are cylindrical, but not of uniform diameter throughout; and the silk fibers are uniform cylinders.

The animal fibers, wool and silk, may be distinguished from the plant fibers by the following chemical tests: Both wool and silk are completely destroyed by the action of a

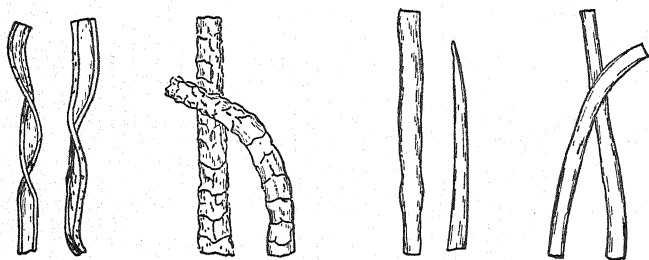


FIG. 374. — Fibers of cotton, wool, linen, and silk.

hot solution of sodium hydroxide of 5% strength; the plant fibers, cotton and linen, are hardly affected by such treatment. On the other hand, cold concentrated hydrochloric acid has little effect on wool and it dissolves silk slowly, but it attacks the plant fibers and destroys them. It is easy to distinguish cotton from linen by the aid of the microscope, but difficult to tell them apart by chemical tests, if the linen has been laundered a few times. Cold concentrated sulfuric acid destroys cotton in about two minutes, but new linen is only slightly attacked in that time.

*Hemp*, *jute*, and *ramie* are other cellulose fibers used for cordage and for textiles. By chemical treatment, certain fibers may be given entirely different properties. Sometimes they are made more lustrous, sometimes they are strengthened, and sometimes they take dyes more readily. Mercerized cotton and the so-called artificial silks are examples of such products.

**680. Wool.** Wool is an animal fiber, usually obtained from the sheep, some species of goats, or from the llama,



an animal found in the Andes Mountains of South America. Mohair is made from the fleece of the Angora goat, and cashmere from the wool of a goat found in Tibet. Wool contains sulfur and nitrogen in addition to carbon, hydrogen, and oxygen. In scouring wool, suint and lanolin are obtained as by-products. *Suint* is a water-soluble substance rich in potassium compounds. *Lanolin* is a wool-fat that is used in pharmacy as a vehicle for ointments.

Alkalis and oxidizing agents destroy woolen fabrics. Therefore a laundry soap containing much free base is not suitable for washing woolen, and chlorine is too strong an oxidizing agent to be used for bleaching woolen goods. Wool is quite hygroscopic, the amount of moisture adsorbed upon the surface of the fiber being quite marked. Wool is sufficiently basic to combine readily with acid dyes without the use of a mordant. Wool fibers become brittle if heated much above 100° C.

**681. Silk and Its Properties.** Silk also contains nitrogen, but, unlike wool, it does not contain sulfur. Silk is obtained by unwinding the cocoons spun by the silkworm. The silk glue must be softened first in warm water before the fibers can be reeled. Like wool, silk is very hygroscopic. The determination of the amount of such water adsorbed is technically known as *conditioning*. It may amount to as much as 30% of the weight of the silk. To make silk smooth and glossy the raw product, which is quite harsh, is treated with a warm soap solution to dissolve more of the silk glue. If the product is to be *ecru silk*, the washing is continued until the loss of weight is only 2% to 4%. If all the glue is removed the loss in weight may be as much as 25% to 30%. During the dyeing of silks tin salts are often added. Such *weighting* of silk may more than double the weight of a fabric. A silk so heavily *weighted* or *loaded* may crack very quickly.

Silks are readily attacked by alkalis. They dissolve in



hydrochloric acid slowly. Strong oxidizing agents destroy the fiber. Silk is bleached with sulfur dioxide, hydrogen peroxide, or a dilute solution of potassium permanganate.

**682. How Cotton Is Mercerized.** If cotton is immersed in a strong solution of sodium hydroxide, it shrinks to about

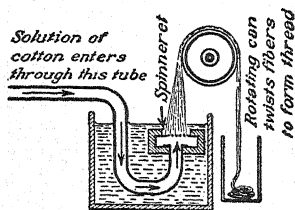


FIG. 375. — The solution of cotton forms a fiber as it flows into the caustic liquid.

three-fourths its former length. But if the cotton is stretched on a frame to prevent shrinkage, the nature of its fiber will be changed when it is immersed in a 34% sodium hydroxide solution. Cotton fibers so treated become stronger and they take on a luster that makes them more closely resemble silk. Cot-

ton so treated is said to be *mercerized*, because the process was devised by John Mercer. Mercerized cotton takes dyes better than ordinary untreated cotton.

**683. Some Silk Substitutes.** Although the name "artificial silk" is given to some cotton products made to resemble silk, yet it is a misnomer. They do not contain silk, and they are not silks made by synthesis. They are made from cellulose, and are now sold under the name "rayon." The various processes used for making these products differ chiefly in the method used to make colloidal suspensions of the cellulose fibers. Generally the short fibers that are unfit for spinning are used for this purpose. They are thoroughly cleaned and dried, and then converted into colloidal suspensions by one of three or four processes: (1) In the *pyroxylin silks*, which were the first manufactured, the cellulose is nitrated by treating it with a mixture of nitric and sulfuric acids. Then a colloidal suspension of the nitrated cellulose is prepared to be used for spinning. Cellulose acetate is sometimes used instead of cellulose nitrate. (2) In the *viscose process* the solution of cellulose is prepared by treating wood

fibers with sodium hydroxide and carbon disulfide. (3) In the *cuprammonium process* the short fibers of cotton are dissolved in an ammoniacal solution of copper. When air is present ammonium hydroxide will dissolve copper, and the solution thus formed dissolves cellulose.

In each process the clarified solution is forced through spinnerets. The spinneret is a thin disc made of an alloy of

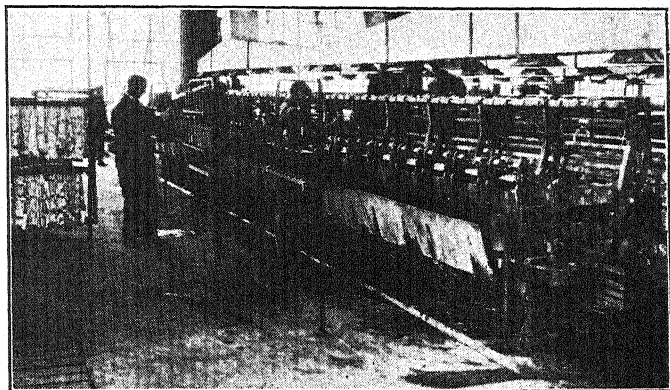


FIG. 376. — Spinning artificial silk.

gold and platinum. In each disc there are twenty or more holes only 0.005 mm. in diameter. As the colloidal suspension is forced out through these holes in the spinnerets, it comes into contact with some liquid, usually acid or alkaline, which precipitates the fiber. (See Fig. 375.) Thus twenty small fibers are produced, and they are twisted together to form a single thread. Figure 376 shows a row of spinning machines used to make "artificial silk," or "rayon." The fibers are then reeled and washed to free them from the acid or alkali used to precipitate the fiber. (See Fig. 377.) The pyroxylin silks are treated with alkaline sulfides to denitrate them so they will be less flammable.

Silk substitutes produced by the processes described are

almost as strong as natural silk, except when they are wet. They take dyes better than does cotton. In some cases they are even more lustrous than real silk.

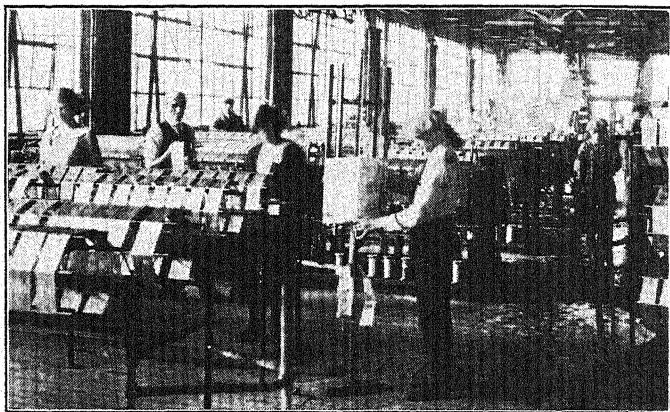


FIG. 377. — Reeling and washing the silk.

#### D. GUMS — RESINS — VARNISHES — LACQUERS

**684. Gums.** Several kinds of trees secrete gummy substances that are exuded from the bark when incisions are made. They are carbohydrates that as a rule dissolve in water and form a mucilage. They are insoluble in alcohol.

*Acacia*, or *gum arabic*, and *gum tragacanth* are two common gums. They find use in preparing emulsions, in confectionary and lozenges, in calico printing, and in finishing cloth. *Cherry gum* finds use for stiffening hats.

**685. Resins.** The resins also contain carbon, hydrogen, and oxygen. They are hard, translucent solids, generally obtained as exudations from certain trees, although they may occur as fossil mineral substances. They differ from the gums, because they are insoluble in water, but they are

generally soluble in alcohol and turpentine. *Rosin, copal, lac, amber, dammar, and sandarac* are important resins. They find use in the varnish industry.

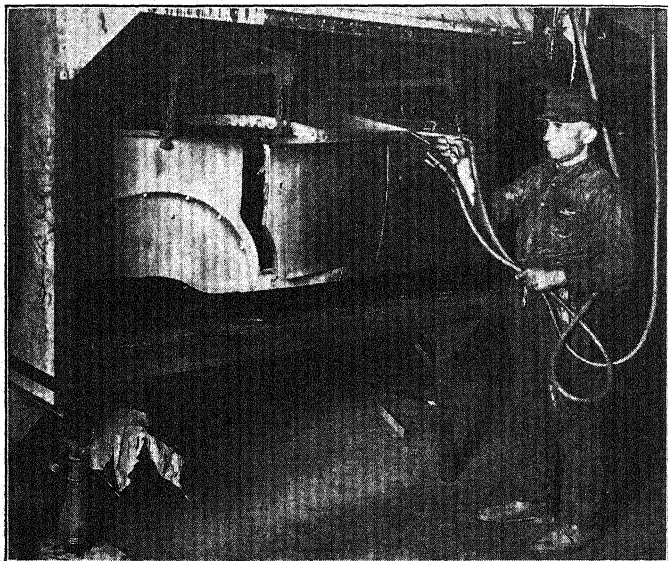
**686. Varnishes** are made by dissolving resins in a suitable solvent. A good varnish should not be discolored by the action of water. It should form a hard, translucent, lustrous coating, tough enough so it will neither crack easily, nor form a resinous dust when scratched with a sharp instrument. The properties depend upon the nature of the resin and upon the solvent used, some varnishes being tough and elastic, others being hard but somewhat brittle.

*Spirit varnishes* are made by dissolving a resin, usually *lac*, in alcohol. Such a varnish is known as *shellac*. It gives a hard surface and dries rapidly as the alcohol evaporates. *Turpentine varnishes* usually give a tougher coating; they are made by dissolving resins in hot turpentine. *Oil varnishes* are made by heating the melted resins with linseed oil or Chinese wood oil. They form excellent varnishes since the coat is very tough and resists the action of water very well. Copal is a resin largely used in making high-grade varnishes, while rosin is employed in the manufacture of cheap varnishes.

**687. Lacquers.** Lacquers are being used more and more instead of varnish and even of paints, especially for furniture and for automobiles. They are less affected by weather conditions than either paints or varnishes. At one time the name lacquer was applied to varnish itself, especially when several coats were applied and baked on the surface. The *modern lacquer* consists of *cellulose nitrate* or *cellulose acetate* dissolved in some solvent such as butyl alcohol, butyl acetate, or acetone. They dry quickly, since the solvent evaporates rapidly and leaves a film of the cellulose nitrate. To keep this film from cracking, either *camphor* or some substitute for it is added to the lacquer. Sometimes one of the varnish resins is added to make the lacquer more lustrous

and to give it a harder surface. Pigments are used to give color to the lacquer, just as they are used in paints.

To apply lacquers a spray gun may be used. (See Fig. 378.) When they were first used, this method of applying them



*Courtesy of Buick Motor Co.*

FIG. 378. — Lacquer may be applied to surfaces by means of a spray machine or gun.

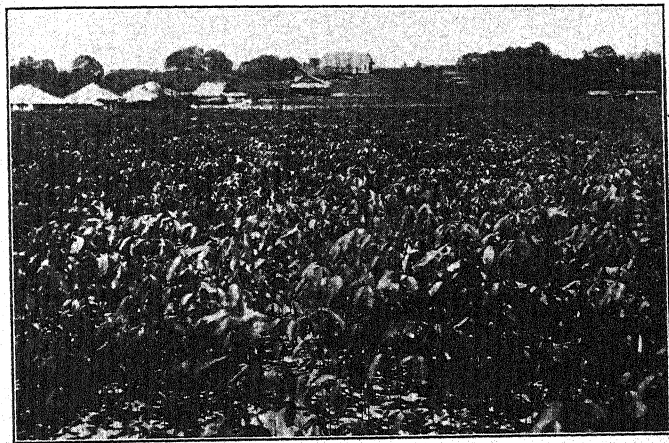
was nearly always used. Now less volatile solvents are in use, and they dry slowly enough so the lacquer may be applied with a brush.

### E. PLASTICS

688. What Is a Plastic? If we mix clay with water, the plastic mass that is formed may be worked, pressed, or molded into any desired shape and then fired to make it hard so it will retain this shape. Glass is so soft when heated

that it may be rolled, pressed, or blown into any form, which is maintained when the glass is cooled. The industrial chemist deals with many plastics, which under some conditions are so soft that they can be molded at will and under other conditions are hard enough to retain their shape.

Glass and clay are plastics that have long been used. Asphalt is a plastic that finds use in insulating lacquers and

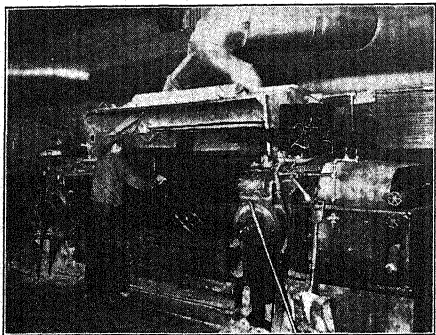


*Courtesy of Firestone Tire and Rubber Co.*

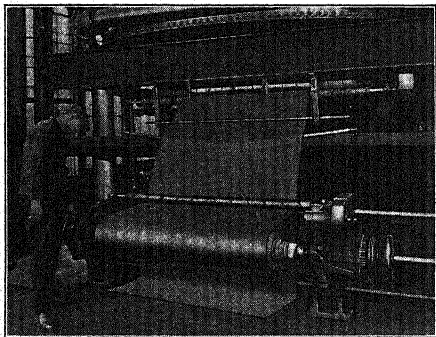
FIG. 379. — A nursery of young rubber plants. In six or seven years, they will grow to a height of about 60 ft., and be ready to tap for rubber.

for making pavement. In a sense the lacquers and varnishes belong to the group of plastics. Other plastics include rubber, bakelite, celluloid, pyralin, cellulose acetate, and guttapercha.

**689. How Rubber Is Made.** Several different kinds of trees that grow in tropical climates produce a milky sap which consists of water with small particles of rubber dispersed in it. The cultivated trees in Brazil, Peru, Africa, and the East Indian Islands are tapped and this sap, which is called *latex*, is collected in cups or buckets. (See Figs. 379



The latex from the rubber trees is treated with acetic acid to precipitate the rubber. Then the rubber is cut into strips, washed and milled to make it into plastic form ready for combining with the cord fabric. The huge rollers shown at your left in Fig. 381 are used to prepare the rubber for use in making cord tires for use on automobiles.



After the rubber has been cleansed and then thoroughly mixed with such substances as zinc oxide, lithopone, carbon black, and sulfur, it is converted into liquid form. Figure 382, shown at your left, represents one of the machines for dipping the cord fabric into the liquid. The rubber penetrates the fabric and insulates each fiber. Glue is sometimes added, too.

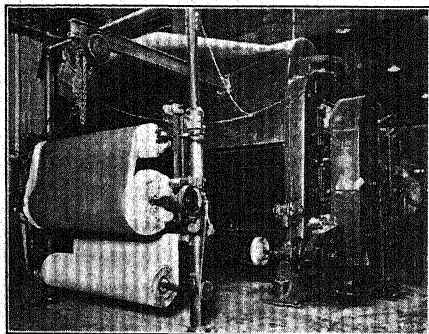
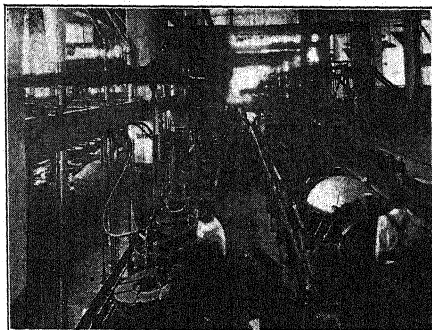


Figure 383 shows a giant calender machine used by one of the manufacturers of automobile tires to make the rubber and cords into one integral piece. The cord fabric, after the gum-dipping, is passed between large steam-heated rollers under sufficient pressure to thoroughly impregnate the cords with the rubber. This process is called calendering.



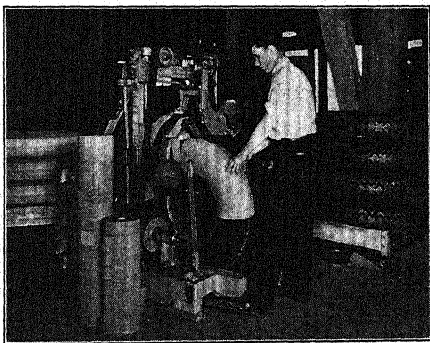
After the cord has been thoroughly impregnated, the casing is built up either by winding the rubber-impregnated cord on an iron wheel, or by winding it on a drum and then forcing it into the desired size and shape. Figure 384 at your right shows workman putting a casing into a mold.



In the mold the tires are heated under steam pressure. The heat vulcanizes the "green" tire and at the same time the tread design is impressed upon it. This part of the operation is entirely automatic. After the tires are removed from the mold, they are given a final inspection, as shown in Fig. 385.



The tires are then cleaned and marked as to quality. To protect the tire so it will be received in good condition by the consumer, it is wrapped completely with heavy paper. Figure 386 shows the tires being wrapped for shipment.



and 380.) In the older process, the milky juice was collected on the end of a stick and heated over a smoky flame to evaporate the water. In the modern process of making rubber, acetic acid is added to the latex to precipitate the rubber. (See Figs. 381 to 386.) The rubber is then cut into strips, and washed and kneaded thoroughly to free it from impurities.

Rubber is a hydrocarbon whose simplest formula is  $C_5H_8$ . It can be made in the laboratory synthetically, but it is



Courtesy of Firestone Tire and Rubber Co.

FIG. 380. — Tapping a rubber tree and collecting the latex.

cheaper to produce it from plants. The pure rubber is so sticky and soft in warm weather that it cannot be used alone. Years ago manufacturers tried to make water-proof garments and boots out of rubber, but in hot weather they were really "gum" boots, and in cold weather a rubber-coated garment became stiff enough to stand alone. In 1839 Charles Goodyear, an American inventor, learned how to vulcanize rubber by heat-

ing it with sulfur. The addition of the sulfur gives the product the desired plasticity and elasticity.

**690. Bakelite.** An interesting plastic is produced by treating formaldehyde with phenol, or carbohic acid. From the name of the inventor, L. H. Baekeland, a Belgian-American chemist, this product is called *bakelite*. One form of bakelite is soluble and fusible. Another type is soluble but infusible, and a third type neither fuses nor dissolves. A new form which reacts with vegetable oils to make paints and varnishes having the resistance and permanence of the

alkaloid extracted from cinchona trees. Its hydrobromide and sulfate are extensively used in medicine, especially in the treatment of malaria. *Cocaine*, obtained from coca leaves, is an important local anesthetic. *Caffeine* is an active stimulant found in coffee and tea. *Codeine* is an alkaloid extracted from opium, as is *morphine*. Both alkaloids are used to allay pain. Paregoric and laudanum are prepared from opium. *Nicotine* is a very poisonous compound found in tobacco. *Strychnine* is an active poison that occurs in *nux vomica*. *Atropine* is an alkaloid found in belladonna. It is used by optometrists to dilate the pupil of the eye. *Ptomaines* are alkaloids formed in dead animal tissues.

While such alkaloids as morphine and cocaine are very valuable drugs, they should never be used unless prescribed by a physician, since they are habit-forming drugs.

#### I. POISONS AND ANTIDOTES

**704. Poisons and Antidotes.** In addition to the alkaloids mentioned in the preceding section, many metallic compounds are poisonous. In fact, soluble compounds of arsenic, antimony, barium, zinc, tin, lead, copper, mercury, and silver are all more or less active poisons. Several phosphorus compounds are poisonous, and certain groups of elements like the cyanide group are extremely poisonous.

An *antidote* is some substance used to counteract a poison. It may destroy the effect of the poison by neutralization, or it may unite with it to form an insoluble compound which is not absorbed by the digestive tract. Three general rules may be given that should be followed in case of poisoning. (1) Give an emetic to produce vomiting. Ipecac is usually most successful, as it contains the alkaloid *emetine*, a very nauseating compound. (2) Give an antidote, if the nature of the poison is known. (3) Give a purgative, such as castor oil or Epsom salts, to remove the poison from the intestines. Very often the poison is unknown and no special antidote

can be given. Fortunately albumin forms an insoluble compound with the salts of most metals, and the whites of eggs and milk may be used freely, as the treatment can do no harm. If a *narcotic* poison, such as *opium*, *morphine*, or *nicotine*, has been taken, a stimulant like strong coffee should be given in quantity. *Alcohol is not a stimulant, but a narcotic.* In any case, do not let the person sleep, but keep him moving. The inhalation of ammonia is beneficial. For a *stimulant* poison like *strychnine*, a sedative such as sodium bromide may be used, or a narcotic like chloral.

For *acid* poisoning, use sodium bicarbonate, soapsuds, chalk, or magnesia.

For *alkali* poisoning, use vinegar, lemon juice, or orange juice.

*Arsenic.* Milk; raw eggs; freshly precipitated ferric hydroxide. Such rat poisons as "rough on rats" contain arsenic, as does also Paris green.

*Bichloride of Mercury.* For this and other mercury compounds, use milk freely; white of eggs; zinc sulfate.

*Carbolic Acid.* Alcohol; raw eggs; Epsom salts.

*Hydrocyanic Acid.* Ferrous sulfate followed by small quantities of potassium carbonate; artificial respiration; inhaling ammonia.

*Iodine.* Starchy foods in abundance; "hypo."

*Lead Salts.* Epsom salts; milk; albumin.

*Phosphorus.* Copper sulfate; Epsom salts. Avoid oils.

*Potassium Cyanide.* Ferrous sulfate. Artificial respiration.

*Silver Nitrate.* Sodium chloride, or common table salt.

*Tartar Emetic.* Milk; eggs.

## SUMMARY

The *carbohydrates* contain *carbon*, *hydrogen*, and *oxygen*; they include sugars, starch, cellulose, dextrine, and certain gums.

Cane sugar, beet sugar, and maple sugar all contain sucrose,

$C_{12}H_{22}O_{11}$ . When sucrose is heated to  $210^{\circ} C.$ , it is converted into *caramel*. When treated with acids *inversion* occurs, resulting in the formation of dextrose and levulose. These sugars are *isomeric*; they have the same formula, the same molecular weight, but differ in properties.

*Lactose*, or milk sugar, contains water of crystallization. All the sugars are used as foods.

*Starch* is a white amorphous substance made by plants that have green coloring matter. It is a good food, it finds use in the laundry, and in finishing cloth. With iodine it produces a blue-black color.

*Cellulose* forms the framework for woody plants. It is used in the textile industry, for making explosives, paper, celluloid, and rayon.

*Dextrine* is made from starch. It finds use as a mucilage and in calico printing.

*Gums* and *resins* also contain carbon, hydrogen, and oxygen. The gums are *water soluble* or at least partially so, but *insoluble* in alcohol. The reverse is true of the resins. Resins are used in the varnish industry. Spirit varnishes consist of shellac dissolved in alcohol. Turpentine varnishes consist of turpentine in which a resin has been dissolved. Oil varnishes are made from linseed oil or China wood oil and such resins as copal, amber, dammar, and sandarac. Rosin is used in cheap varnishes.

A substance taken into the body that supplies to it heat, energy, or nourishment is termed a *food*. Digestion is the process of changing insoluble foods into soluble compounds.

Carbohydrates, proteins, and fats or oils form the *three classes* of nutrients needed by the body. Mineral matter is also essential to the body.

The value of a food may be determined by the number of calories it yields upon oxidation, by the relative proportion of the three nutrients it contains, by the ease with which it is digested, by the amount of indigestible matter, and by its liability to ferment. It must contain vitamins.

Foods are cooked to make them more palatable, to promote digestion, and to destroy any bacteria that may be present. Baking, roasting, and boiling are all excellent methods of cooking foods.

*Bacteria*, *yeasts*, and *molds* are three types of microorganisms that cause food to ferment or decay. They thrive at moderate temperature, on a moist surface, protected from sunlight, provided they have plenty of food material.

Foods are preserved by destroying these organisms and preventing their coming into contact with the food thus sterilized. The various methods include *drying*, *canning*, *preserving with sugar*, *pickling*, *salting* and *smoking*, *cold storage*, and the use of *chemical preservatives*.

A substance mixed with a food to increase its weight or its bulk is termed an *adulterant*. Chemical preservatives are often classed as adulterants. The adulterant used is always some cheaper product.

Both *disinfectants* and *antiseptics* destroy bacteria that produce disease. *Antiseptics* are of such a nature they may be applied to living tissues.

An *alkaloid* is a nitrogenous compound obtained from plants. Some alkaloids find use in medicine.

An *antidote* is a substance used to counteract a poison. In case of poisoning give an *emetic*, then an *antidote* if possible, and follow with a *cathartic* to remove the poison from the intestines.

## QUESTIONS

### GROUP A

1. What is a carbohydrate? Name at least three, giving their formulas.
2. What is meant by the inversion of sugar? How is it produced?
3. Discuss the commercial importance of cellulose.
4. What is meant by loading paper? By sizing paper?
5. How would you distinguish cotton from linen? Cotton from wool? Wool from silk? Silk from rayon?
6. Why should a proper menu contain all the various food nutrients?
7. What purpose does each of the three nutrients serve in the body?
8. What is the objection to eating raw potatoes? Raw meats?

9. Outline several methods of preserving foods. Upon what principle is each method based?
10. What principles are involved in the use of antidotes to poisons?

GROUP B

11. Why is vinegar added to a candy that is to be pulled? Would it do as well to start with glucose?
12. How does "smokeless powder" differ from pyroxylin silk?
13. What are the characteristics of a good varnish? How would you test a varnish?
14. Why do we relish buckwheat cakes with butter and syrup more in January than in July?
15. Why are chemical food preservatives also good antiseptics?
16. Give examples of several food adulterants.





## APPENDIX B

### BAROMETER CORRECTIONS

**How to Correct Barometer Readings.** 1. *When levels cannot be adjusted.* In collecting gases by liquid displacement, it is customary to adjust the levels if the volume of the gas is to be measured. Sometimes this is impossible, and then the reading of the barometer must be corrected.

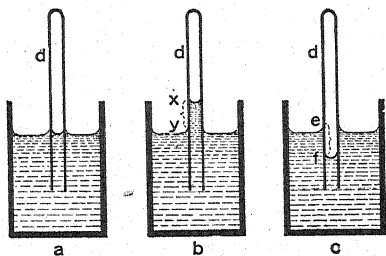


FIG. 391. — Difference of levels.

In Fig. 391a, the liquid in the tube stands at the same height as that outside. Therefore the gas *d* is exerting the same pressure that the air does outside. We know that the pressure which the gas sustains can be found by reading the

barometer, and that no correction is necessary.

If we refer to Fig. 391b, we see that the pressure which the gas *d* sustains is less than the barometer reading, for it requires the gas pressure plus the weight of the column of liquid *xy* to equal the pressure outside. Suppose the gas is collected over mercury and *xy* is 60 mm. high. If the barometer reads 740 mm., then the gas pressure of *d* plus 60 mm. = 740 mm. The gas *d* alone exerts a pressure of 740 mm. - 60 mm., or 680 mm. In solving any problem for change in pressure on this gas, we would use as the original pressure 680 mm. If the gas had been collected over water and *xy* were a water column 68 mm. long, then we would not have

*subtracted* 68 mm. from the barometer reading, but 68 divided by 13.6, since mercury is 13.6 times as heavy as water. The *true* pressure of the gas in such case would be 735 mm. ( $740 - \frac{68}{13.6}$ ).

In Fig. 391c the gas *d* exerts a pressure greater than that of the atmosphere by a column of liquid *ef*. In this case the reading as shown by the barometer must be corrected by *adding* as many millimeters as *ef* measures, if the liquid is mercury, or the number of millimeters divided by 13.6, if the liquid is water. To find the correct pressure the gas exerts when the inside level is the *higher* of the two we must *subtract* from the barometer reading the length of the column *xy* if the liquid used is mercury. If the inside level is *lower* than the outside one, we must *add* to the barometer reading the length of the column *ef* as a correction. If the liquid used is *water* as is usually the case, the length of the water column divided by 13.6 (since mercury is 13.6 times as heavy as water) must be *subtracted* from or *added* to the barometer reading as above.

PROBLEM: A gas collected over mercury measures 40 c.c. when the mercury stands 90 mm. higher in the tube than outside; the temperature is 18° C., and the barometer reading 755 mm. What volume will the gas occupy at standard temperature and pressure?

SOLUTION: The barometer reading corrected for difference of levels equals 755 mm. less 90 mm., or 665 mm. This is the real pressure upon the gas. The corrected volume is then found as follows:  $40 \text{ c.c.} \times \frac{273}{291} \times \frac{665}{760} = 32.8 \text{ c.c.}$

2. *When the gas contains water vapor.* When gases are collected over water, they will be moist because water has been evaporating at the same time. After a time the gas standing above the water becomes saturated with water vapor. The amount of water vapor needed to saturate a gas depends upon the temperature. See Table 3 in Appendix A. When evaporation occurs in this manner, the vapor

exerts a pressure upon the liquid. Suppose we let a bottle of oxygen gas stand over water as in Fig. 392 until it is saturated with water vapor. Suppose the temperature is  $26^{\circ}\text{C}$ . and the barometer reads 775 mm. The pressure of the oxygen gas plus the pressure of the water vapor (25 mm. as shown in Table 3) equals 775 mm. The pressure of the oxygen alone is equal to 775 mm. - 25 mm., or 750 mm. Therefore, if we wish to find the volume of a *dry* gas we must always *subtract* from the barometer reading the pressure which the water vapor exerts.

**PROBLEM:** Four hundred c.c. of oxygen are collected over water. The temperature is  $20^{\circ}\text{C}$ ., and the barometer reads 750 mm. Find what volume the *dry* oxygen will have at standard temperature and pressure.

**SOLUTION:** From the table we find that at  $20^{\circ}\text{C}$ ., water vapor exerts a pressure equal to 17.4 mm. of mercury. Then the oxygen gas alone is exerting a pressure of 750 mm. less 17.4 mm., or 732.6 mm. This part of the operation is generally spoken of as correcting the barometer reading for pressure due to water vapor. The volume of oxygen at standard conditions may now be found by using the following equation:  $400\text{ c.c.} \times \frac{732.6}{760} \times \frac{273}{293} = 359\text{ c.c.}$

Very often a correction for both aqueous pressure and difference of levels is necessary as in the following problem:

**PROBLEM:** A gas collected in a tube over water measures 75 c.c. when the outside level is 68 mm. higher than the inner; the temperature is  $20^{\circ}\text{C}$ . and the barometer reads 757.4 mm. Find the volume of the *dry* gas at standard temperature and pressure.

**SOLUTION:** The barometer reading corrected for aqueous pressure equals 757.4 mm. - 17.4 mm., or 740 mm. The correction

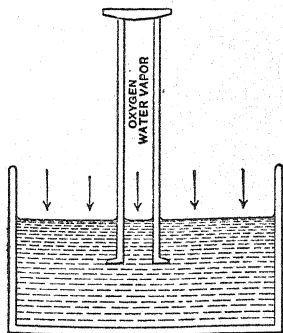


FIG. 392. — The combined pressure of the oxygen and water vapor equals the pressure of the atmosphere.

to be *added* for difference of levels is  $\frac{6.8}{13.6}$ , or 5 mm. The *true* pressure of the gas is 740 mm. plus 5 mm., or 745 mm. Solving by the use of the laws of Boyle and Charles,

$$75 \text{ c.c.} \times \frac{745}{760} \times \frac{273}{293} = \text{new volume.} \quad \text{The result is 69.2 c.c.}$$

**Arrhenius' Theory Modified.** As new facts are brought to light, theories must often be modified. For weak electrolytes the theory needs no change, but strong electrolytes are now believed to be practically 100% dissociated. The methods used to determine the degree of ionization work very well for weak electrolytes, but not for strong electrolytes.

The modern view concerning acids assumes that the hydrogen ion,  $\text{H}^+$ , cannot exist alone in solution. The loss of an electron by the hydrogen atom leaves a *proton particle*. Such a small particle, positively charged, would combine with water to form the *oxonium* ion  $\text{H}_3\text{O}^+$ , or  $\text{H}_2\text{O} \cdot \text{H}^+$ . The true positive ion consists of a molecule of the solvent combined with one proton. In this revised theory, an acid is a *giver of protons*, and a base is a *receiver of protons*.

**What Is Meant by the pH Value?** Some indicators are much more sensitive to acidity or to alkalinity than others. In order to have a definite standard, chemists now use the hydrogen-ion scale, which has for its unit the *pH value*. With this scale, a neutral substance such as water has a pH value of 7. Any acid substance has a lower pH value than water. For example, a substance which has an acidity ten times as great as that of water has a pH value of 6. A pH value of 5 shows a solution that is ten times as strongly acid as one having a pH value of 6. A pH value of 8 is used to represent a substance ten times as strongly alkaline as one with a pH value of 7. Indicators have been prepared that show color shades which correspond to the whole range of pH values. The acidity or alkalinity of a solution is determined by using the same indicator and matching its color with one in the series. That gives its pH value.

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